329. *Reversible Replacement of Aromatic Halogen Atoms.*

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Suitable conditions have been found for the interchange of chlorine, bromine, and iodine atoms in the halogeno-2 : 4-dinitrobenzenes. Iododinitrobenzene may be prepared by heating chlorodinitrobenzene with sodium iodide in boiling ethylene glycol.

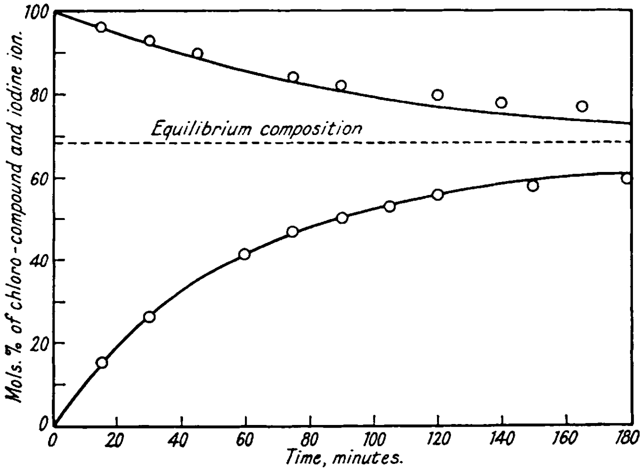
This and the similar reaction of chlorodinitrobenzene with a bromide are reversible. These reactions have been followed in both directions, and measurements of the velocities and the positions of equilibrium have been made.

Although the ready displacement of the halogen atom in halogeno-2 : 4-dinitrobenzenes by various reagents is well known, the action of halogen ions has not hitherto been observed. The rapid conversion of chlorotrinitrobenzene into the iodo-compound by a hot alcoholic solution of potassium iodide was recorded by Hepp (*Annalen*, 1882, **215**, 344), but chlorodinitrobenzene is not affected by this reagent even after long boiling. We find, however, that sodium iodide acts rapidly on this substance in boiling ethylene glycol, and iodo-2 : 4-dinitrobenzene may be conveniently prepared by this method. Moreover, iododinitrobenzene is quickly converted into the chloro-compound under similar conditions by an excess of (lithium) chloride.

The analogous reaction of chlorodinitrobenzene with sodium bromide in hot ethylene glycol is incomplete, the concentration of bromion being limited by the solubility of the salt, but the bromo-compound readily yields the pure chloro-compound in presence of lithium chloride. Iododinitrobenzene may be similarly converted into bromodinitrobenzene. On the other hand, an attempt to introduce a fluorine atom was not successful, silver fluoride yielding with the chloro-compound only 2 : 4-dinitrophenol, and this was also the only product isolated when dinitrophenyl *p*-toluenesulphonate was heated with a chloride in boiling glycol.

A similar reversible reaction takes place between 1 : 3-dichloro-4 : 6-dinitrobenzene and an iodide in hot glycol, the product being a mixture from which the di-iodo-compound may be separated by crystallisation. The reaction of an iodide with 3-chloro-4 : 6-dinitrotoluene is also incomplete, the product being a mixture containing about 70% of 3-*iodo*-4 : 6-*dinitrotoluene*, a substance readily obtained by nitrating *m*-iodotoluene.

In order to study the reversibility of this type of reaction, the course of the change $C_6H_3(NO_2)_2I + Cl' \rightleftharpoons C_6H_3(NO_2)_2Cl + I'$ in ethylene glycol solution at 175° has been followed in both directions by determining the iodine ion and applying the general formula for a reversible second-order reaction to the resulting data (compare J., 1931, 2957). The results, which are illustrated in the figure, show that the reaction is in fact a reversible bimolecular one, and that with molar quantities it proceeds at 175° from either side towards an equilibrium at 68 mols. % of chlorodinitrobenzene and iodide. At this temperature prolonged heating causes some subsidiary reaction to set in, probably involving reduction, and consequent deactivation of the reactive halogen atom. The equilibrium figure is therefore not quite reached from each side, but the value selected by graphical extrapolation is in fair agreement with that deduced from the velocities in opposite directions of $4{\cdot}58 \times 10^{-2}$ and $1{\cdot}01 \times 10^{-2}$ l. g.-mol.$^{-1}$ min.$^{-1}$, and it also leads to coefficients which are approximately constant through the main part of the change.



Reversible reaction $C_6H_3(NO_2)_2I + Cl' = C_6H_3(NO_2)_2Cl + I'$.
(The points are experimental: the curves are calculated.)

The reaction was also followed in one direction at 165°, the velocity coefficient being $2{\cdot}21 \times 10^{-2}$ and the (computed) equilibrium at 64 mols. % of chloro-compound. The temperature coefficient of velocity per 10° of 2·07 indicates an activation energy of the order 28 kg.-cals.

An examination has also been made of the interaction of bromodinitrobenzene and chlorion in hot ethylene glycol, the course of the reaction being followed by observations of the density of a 25% solution of the recovered organic material in nitrobenzene, and an empirical reference curve being used. At 175° the equimolar mixture tends from either side to an equilibrium with 23 mols. % of bromo-compound, the forward and the reverse reaction having velocities of $3{\cdot}71 \times 10^{-2}$ and $3{\cdot}26 \times 10^{-3}$ l. g.-mol.$^{-1}$ min.$^{-1}$ respectively. Direct determination of the equilibrium proportions at 195° again showed a value of 23 mols. % of bromo-compound.

An independent test was made of this equilibrium, in connexion with which we have to thank Mr. J. E. Caygill, of Rochdale Technical School, for his assistance. Chloro- or bromo-dinitrobenzene was stirred in glycol solution at 190° with an excess of both sodium chloride and sodium bromide until equilibrium had been reached. This must clearly be determined by the saturation solubilities of the two solid salts present. The silver halides precipitated from the diluted reaction mixture contained 96·1 mols. % of bromide. This, together with the equilibrium constant derived from the velocity observations, requires that the organic material should contain 68·7 mols. % of bromodinitrobenzene, whereas 69·1 mols. % were actually found.

EXPERIMENTAL.

*Preparation of Iodo-*2 : 4*-dinitrobenzene from Chloro-*2 : 4*-dinitrobenzene.*—The chloro-compound was heated with sodium iodide (5 mols.) in boiling glycol for ½ hour, and the mixture poured into water. The product was pure after crystallising once from ethyl alcohol and once from petroleum (b. p. 90—120°) (yield, 30%).

Action of Sodium Iodide on 4 : 6*-Dichloro-*1 : 3*-dinitrobenzene.*—The two substances were heated in boiling glycol for 5 mins. The product, once crystallised from ethyl alcohol, had m. p. 143° (the dichloro-compound has m. p. 102°). After six further crystallisations from the same solvent, the material had m. p. 155° and was nearly pure di-iododinitrobenzene (Found : I, 59·4. Calc. : I, 60·5%). Boiling aniline converted this into the dianilinodinitrobenzene (yield, 76%), which was pure after one crystallisation (m. p. 186°) and was identical with the substance prepared from the dichloro-compound.

Action of Sodium Iodide on 3*-Chloro-*4 : 6*-dinitrotoluene.*—The chloro-compound was heated with a boiling saturated solution of sodium iodide in glycol for 5—30 mins. The product, crystallised from ethyl alcohol, had m. p. 98—101° and was a mixture (0·2674 G. gave 0·1958 g. of AgCl + AgI. Calc., for chloro-compound : 0·177 g. of AgCl. Calc., for iodo-compound : 0·204 g. of AgI). Repeated crystallisation did not separate the pure 3*-iodo-*4 : 6*-dinitrotoluene*, but this was readily prepared by warming *m*-iodotoluene with an excess of nitrating mixture. The product, crystallised from glacial acetic acid, formed sulphur-yellow prisms, m. p. 108° (Found : C, 27·6; H, 1·6; I, 41·9. $C_7H_5O_4N_2I$ requires C, 27·3; H, 1·6; I, 41·3%).

Reversible Displacement of Iodine by Chlorion.—The iodo- and the chloro-dinitrobenzene were recrystallised several times. Pure anhydrous lithium chloride or iodide was used, and the concentrations of the solutions checked by titration. The materials were weighed into separate test-tubes, which were placed in a large, well-stirred oil-bath heated electrically and controlled to ±0·4°. At intervals a tube was removed, the contents diluted, filtered, and the iodine ion determined by Lang's method (*Z. anorg. Chem.*, 1922, **122**, 332). In the reverse reaction it was found more practicable to use the same method of titration than to remove the iodide and titrate the chlorion remaining.

(i) *Iododinitrobenzene with chlorion at* 165°.

Concentrations of iodo-compound (*a*) and of chloride (*b*) each 0·370 mol. per l. (these figures are corrected for the expansion of the solutions, which was separately determined by means of a dilatometer). The coefficient k_1 is calculated by the formula of Bennett and Mosses (J., 1931, 2956).

t (mins.)	8	30	45	60	80	100	120	150	180
x	0·021	0·070	0·099	0·121	0·143	0·159	0·170	0·188	0·204
$k_1 \times 10^2$	—	2·14	2·27	2·28	2·25	2·19	2·09	2·14	2·29

Equilibrium constant, $K = 3{\cdot}10$; n (computed) = 0·236. Mean $k_1 = 2{\cdot}21 \times 10^{-2}$.

(ii) *Iodo-compound with chlorion at* 175°.

$a = b = 0{\cdot}263$ mol. per l.

t (mins.)	15	30	60	75	90	105	120	
x	0·040	0·069	0·109	0·122	0·132	0·137	0·144	
$k_1 \times 10^2$	4·56	4·55	4·66	4·65	4·62	4·34	4·68	Mean 4·58

Equilibrium constant, $K = 4{\cdot}1$; $n = 0{\cdot}179$.

(iii) *Chloro-compound with iodine ion at* 175°.

$a = b = 0{\cdot}260$ mol. per l.

t (mins.)	15	30	45	75	90	120	
x	0·010	0·019	0·027	0·041	0·047	0·053	
$k_2 \times 10^2$	1·03	1·01	1·00	1·01	1·01	(0·91)	Mean 1·01

Equilibrium constant, $K = 4{\cdot}1$; $n = 0{\cdot}084$.

The change of equilibrium with temperature implies a heat of reaction of 10·8 kg.-cals., but the indirect method by which each equilibrium constant was arrived at makes this figure very uncertain.

Reversible Interchange of Chlorine and Bromine.—For the determination of the extent of the reaction between bromodinitrobenzene and chlorion the organic material in the glycol solutions was precipitated by water, taken up in benzene, the solution evaporated, and the residue finally left in a vacuum desiccator. The material was then dissolved to form a 25% solution in nitrobenzene, and the mass of this solution contained in a certain pyknometer at 25° determined. The composition of the organic material was then read from an empirical curve (which was a straight line) representing the corresponding masses of 25% nitrobenzene solutions made from artificial mixtures of chloro- and bromo-dinitrobenzenes heated in glycol (in the absence of salts) and recovered as described above. The figures obtained by this somewhat elaborate method are subject to considerable irregularity, but they suffice nevertheless to show the course of the reaction.

(i) *Bromodinitrobenzene and lithium chloride at* 175° *in glycol.*

$a = b = 0{\cdot}258$ mol. per l.

t (mins.)	15	30	60	120	162	170	∞
x	0·036	0·047	0·102	0·136	0·150	0·155	(0·199)
$k_1 \times 10^2$	4·19	2·88	4·26	3·76	3·52	3·67	Mean 3·71

Equilibrium constant, $K = 11{\cdot}2$.

(ii) *Chlorodinitrobenzene and lithium bromide at* 175°.

$a = b = 0{\cdot}256$ mol. per l.

t (mins.)	30	60	90	120	180	210	∞
x	0·015	0·021	0·026	0·028	0·038	0·042	(0·059)
$k_2 \times 10^3$	4·35	3·32	2·97	3·28	2·74	2·88	Mean 3·26

Equilibrium constant, $K = 11{\cdot}2$.

(iii) *Equilibrium at* 195°. Bromodinitrobenzene was heated with an equimolar quantity of chloride, and chlorodinitrobenzene similarly with bromide, in glycol at 195° for 2 hours. The composition of the organic material in the two cases was 25% and 21% of bromo-compound respectively. The equilibrium figure is therefore taken to be 23%, whence $K = 11{\cdot}2$. Since this figure is identical with that found for 175°, the heat of reaction is zero or small.

(iv) *Equilibrium in presence of glycol saturated with sodium chloride and bromide.* The chloro- and the bromo-dinitrobenzene, recrystallised several times, had m. p. 50·2° and 71·9°. The m. p.'s of mixtures lay within 0·1° on a straight line between these values. The two compounds were separately stirred at 190° in pure ethylene glycol with an excess of dry pure sodium chloride and sodium bromide for 2 hours. Intermediate tests confirmed the approach to an equilibrium from each side. The whole was then poured into water. Mixed halides were precipitated from the aqueous solution, and 0·4374 g. of dry silver salts gave 0·3370 g. of silver chloride on gentle fusion in dry chlorine; hence, silver bromide = 97·01% by weight or 96·1 mols. %. The recovered organic material had m. p. 67·3°, indicating 26·8% of chloro-compound or 30·9 mols. %. A determination of carbon showed C, 30·73 (Calc. for chloro-compound, 35·55; for bromo-compound, 29·15; whence chloro-compound is 24·7%).

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