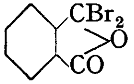
305. *The Tautomerism of Phthalyl Bromide.*

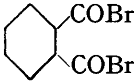
By William Davies, Arthur N. Hambly, and George S. C. Semmens.

It has been shown (Dann, Davies, Hambly, Paul, and Semmens, this vol., p. 15) that phthalyl fluoride exists only in the acyclic form, which is stable, whereas two isomeric forms of phthalyl chloride are known (Ott, *Annalen*, 1912, **392**, 274). As in the phthalyl series the presence of the small and light fluorine atom does not apparently favour tautomerism, the effect of the large and heavy bromine atom has been considered.

Phthalyl bromide is obtained (*a*) by the action of phthalic anhydride in a sealed tube on a mixture of phosphorus penta- and tri-bromides, the latter being used as a solvent and also to reduce the pressure due to the dissociation of the pentabromide, and (*b*) by the action of dry hydrogen bromide on ordinary phthalyl chloride. The purified product in each case has m. p. 78—81° when rapidly taken, but the melting point is never sharp, and when very slowly taken is considerably lower than this. Unqualified references to "phthalyl bromide" apply to this crystalline form and not to any liquid or recently liquid forms of phthalyl bromide. The crystals, m. p. 78—81°, have the cyclic formula (I), and when kept in the molten state for a few minutes are converted into the acyclic form (II), the reverse change spontaneously taking place on cooling. It has not so far been possible to obtain the form (II) in a homogeneous crystalline state, but the liquid form at 90° is (II), and this structure persists for a short time when the liquid form is cooled to the ordinary temperature. Crystalline phthalyl bromide which has been heated to about 90° either alone or in the presence of solvents is remarkably slow in solidifying again on cooling, even in the presence of a small amount of the original bromide in a crystalline condition. The rate of crystallisation is also very variable.



(I.)



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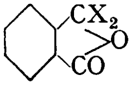

(III.)

Evidence for the constitution of phthalyl bromide and for the tautomeric change to the liquid form has been obtained in four ways.

(1) By a study of the rate of the "unimolecular" reaction at 30° of excess of *iso*propyl alcohol with phthalyl bromide, *terephthalyl bromide*, benzoyl chloride, benzoyl bromide, and acyclic phthalyl chloride. Phthalyl bromide is about one-sixth as reactive as acyclic phthalyl chloride (as II), whereas benzoyl bromide is about ninety times as reactive as benzoyl chloride. This indication of the lactonic structure of phthalyl bromide is supported by the extreme reactivity of terephthalyl bromide, which can exist only in the ·COBr form.

(2) By the change in the rate of reaction with *iso*propyl alcohol at 30° brought about through the previous heating of the bromide. Phthalyl bromide, after being heated at 100° for 30 minutes and then kept at room temperature for 20 minutes, has its activity enormously increased, more than the first half of the curve almost overlapping the curve for terephthalyl bromide. When the cooling period is longer, the rate of reaction is decreased, and finally ordinary crystalline relatively inert phthalyl bromide is obtained from this active liquid form on prolonged cooling. A study of the respective reaction velocity curves in the figure shows that crystalline phthalyl bromide is (I), which changes to the active form (II) on heating, and the less active form is again slowly produced on cooling and long standing. It has not been found possible to follow the change from one form to the other in concentrated toluene solutions by means of refractive index determinations.

(3) By parachor investigations of the structure of liquid phthalyl bromide. The parachor at 90° is 405·2, 405·3, whereas theory requires 390·2 for (I) and 404·9 for (II). It is evident that the liquid phthalyl bromide at 90° has the acyclic formula. The change to this form takes place in a few minutes and is apparently complete, whereas cyclic phthalyl chloride (Sugden, "The Parachor and Valency," p. 47) changes only very slowly to the acyclic form during parachor determinations at 90°.

(4) By a study of chemical evidence, though some of this is not very decisive. The method of Pfeiffer (*Ber.*, 1922, **55**, 415) for discriminating between the two forms of phthalyl chloride is useless when applied to crystalline and liquid phthalyl bromides, and the method used by von Braun (*ibid.*, p. 1308) does not give very definite results (see p. 1313). These methods, which are recommended as useful in deciding the structure of phthalyl types, are both useless in elucidating the still unknown structure of the two phthalyl azides (Lindemann and Schultheis, *Annalen*, 1928, **464**, 244). The action of aluminium bromide on

crystalline phthalyl bromide is also not decisive. A reaction readily takes place, but the only substance which can be isolated (apart from phthalic anhydride), is phthalyl bromide identical with the original material. The regeneration of (I) is to be expected if the original bromide has this formula. The mere fact of a double compound being produced from aluminium halide and a diacyl halide is in itself no criterion of the formula of the latter; *e.g.*, both phthalyl chlorides and both chlorofumaryl and chloromaleyl chlorides form a double compound with aluminium chloride.

The reaction or rather the rate of reaction with aniline is more decisive than the above chemical methods. Unheated, freely dissolved phthalyl bromide is very inert towards aniline in solution during the first few seconds, though on long standing the reaction is practically quantitative. Liquid phthalyl bromide, which has been heated for some time and then rapidly cooled, is very much more reactive than the unheated crystalline form. Owing to the experimental difficulties the quantitative results are very rough (p. **1313**). However, all the chemical evidence available indicates that phthalyl bromide is (I) and the hot liquid form (II).

A survey of what literature is available on the subject of " tautomerism " involving halogen atoms shows that phthalyl bromide is one of the very few halogen compounds showing tautomerism without the intermediate use of metallic complexes formed with molecular quantities of inorganic halides (compare Küster, *Z. physikal. Chem.*, 1895, **18**, 161). The proof of reversible isomeric change is to be found in the different rates of reaction with *iso*propyl alcohol, which vary with the time of keeping the cool, previously heated form. Any catalyst, such as a trace of hydrogen bromide, can hardly be regarded as selective in the production of one form only, as is the presence of a large amount of aluminium chloride in bringing about the conversion of acyclic into cyclic phthalyl chloride, with which the aluminium chloride combines. Therefore, neither phthalyl chloride (Ott, *Annalen*, 1912, **392**, 274) nor the chlorides of anthraquinonecarboxylic acids (Scholl, Dehnert, and Wanka, *Annalen*, 1932, **493**, 56; Scholl, K. H. Meyer, and Winkler, *Annalen*, 1932, **494**, 201), which owe the existence of the second form to the action of aluminium chloride, have yet been proved to show tautomerism despite the claims of the respective authors. Definite instances of indubitable tautomerism involving the " wandering " of a halogen atom are provided by the two " tetrachlorides " of phthalic acid (Ott, *Ber.*, 1922, **55**, 2115), and ethylene and ethylidene bromides (and some other related compounds), between which equilibrium is set up at temperatures above 300° (Sokownin and Zinewsky, *Annalen*, 1907, **354**, 358). The two forms of phthalyl bromide seem more readily interconvertible than the two forms of any other pair of tautomerides where halogen movement is in question.

There seems to be an increasing tendency to tautomerism in the series phthalyl fluoride, chloride, and bromide. It may be an illustration of the Thorpe–Ingold valency deflexion hypothesis, and that increase in size of the substituents X on the CX_2 group in the ring (III) (or the presence of two CCl_2 groups in cyclic phthalic acid " tetrachloride ") enhances the stability of the ring in which these groups occur. But it is much more probable that the tendency noted above is related to another trend. Staudinger and Anthes (*Ber.*, 1913, **46**, 1417) show that the relative ease of hydrolysis of benzoyl chloride, bromide, and iodide with water is in that order. A comparison of the rates of reaction of benzoyl fluoride, chloride, and bromide with *iso*propyl alcohol (p. 1313) shows that benzoyl fluoride also agrees with the generalisation of increasing chemical activity with increasing atomic weight of the halogen. The probability that this order of chemical activity is related to the tendency to tautomerism in the phthalyl series is supported by a consideration of the azides of the two series. Benzoyl azide is much less reactive than benzoyl fluoride, and the two phthalyl azides (Lindemann and Schultheis, *loc. cit.*) show no tendency to tautomerism or even isomeric rearrangement. From a consideration of these facts it is to be expected that phthalyl iodide should show the greatest ease of rearrangement, but this compound decomposes vigorously almost as soon as formed. This work is, however, being continued.

The investigation has shown that the size of the halogen atom in the phthalyl series is not the cause of ease of tautomerism. The essential factor is apparently the chemical activity of the halogen concerned, as shown, for example, with alcohols, and there can be no doubt that the ionising power of the halogen atom and the ease of tautomeric rearrangement are closely related in this series.

EXPERIMENTAL.

Preparation of Phthalyl Bromide.—(1) Phthalic anhydride (14·8 g.) and phosphorus pentabromide (53 g.) are heated with phosphorus tribromide (95 g.), or a mixture of about 100 g. of the tribromide and oxybromide produced in previous experiments, in a sealed tube for 60 hours. The temperature is first kept at 100° for 24 hours, then gradually raised to 165°, and maintained during the final 30 hours at 160—165°. After cooling, the product, which is now at ordinary pressure, is filtered through glass wool and distilled. Phosphorus compounds distil below 145°/24 mm., the next fraction consists of a mixture of phthalic anhydride and phthalyl bromide, and fairly pure *phthalyl bromide* (24 g.; 83%), b. p. 185—193°/24 mm., m. p. 65—75°, is obtained. Recrystallisation from light petroleum (b. p. 60—70°) gives the pure bromide in prisms, m. p. 78—81°.

The temperature recorded for the heating of the sealed tube must be carefully observed. Heating at 100°, rising gradually to 140°, for 82 hours, leaves the phthalic anhydride largely unchanged; if the heating is unduly prolonged, further bromination takes place; and if the temperature is too high, substitution in the nucleus occurs, as is shown by the formation of hydrogen bromide and the presence of non-hydrolysable bromine in the organic material.

(2) This is a more convenient method for the preparation in quantity of phthalyl bromide. Ordinary phthalyl chloride (203 g.; 1 mol.) is exposed at 150—160° to a stream of hydrogen bromide dried over phosphorus pentabromide, and the product soon acquires a bluish-green colour which is lost on distillation. After 28 hours the increase in weight is 65 g. instead of the theoretical 89 g., and, as further bromination is only very slowly brought about, it is advisable at this stage to distil the product through a column. A large initial fraction containing anhydride, unchanged chloride and possibly chlorobromide is obtained up to 134°/2 mm., and the remainder distils almost without residue at 134—142°/2 mm., in about 50% yield. The crystalline bromide has m. p. 78—81° when rapidly taken, though when slowly taken the m. p. is lower, and the bromide can even be liquefied by keeping it at 73° for 15 minutes. The crystalline bromide has b. p. (corr.) 191°/24 mm. and 134°/2 mm., $d_{4^\circ}^{90^\circ}$ 1·809, and is identical (mixed m. p. determination) with the product from method (1). It is very soluble in benzene, and moderately soluble in cold light petroleum. When dissolved in high-boiling petroleum (b. p. 80—100° or higher), it tends to separate as an oil which takes many hours to solidify even after seeding with pure bromide. From low-boiling (below 70°) petroleum the substance separates as crystals much more rapidly.

Analysis. The compound is very readily attacked by moist air, and it is difficult to prevent adventitious moisture forming phthalic anhydride in the process of crystallisation and drying. The amount of phthalic anhydride, when appreciable, can be determined by hydrolysis of the bromide with excess of standard sodium hydroxide, and the bromine by titration of the neutralised solution after Mohr's method, as well as by a Carius determination on the original bromide (Found: C, 32·2, 32·5; H, 1·35, 1·1; Br, 54·3; hydrolysis value, 18·55 c.c. NaOH solution. $C_8H_4O_2Br_2$ requires C, 32·9; H, 1·4; Br, 54·7%; hydrolysis value, 18·7 c.c.).

Reactions. Phthalyl bromide and aluminium bromide. Phthalyl bromide (20 g.) is melted and at once poured on powdered aluminium bromide (25 g.) at 40°. Heat is evolved, the product liquefies and is well shaken and after being kept at 100° for 14 hours is obtained as a brown oil which on cooling readily solidifies. Whilst still warm it is poured on ice, and the ice and organic matter are ground together, extracted with benzene, and dried with sodium sulphate. The benzene after filtration is removed at 30°, and phthalyl bromide is obtained which after recrystallisation has m. p. 78—81° and seems identical with the original compound. A similar result is obtained by varying the proportion of aluminium bromide, and varying the time of heating the mixture from 1½ to 15 hours. In all cases the phthalyl bromide is largely converted into phthalic anhydride even when a mixture of calcium bromide and ice in a freezing mixture is used to decompose the aluminium bromide double compound.

With regard to the following reactions the term "phthalyl bromide" refers to material which has been solid for several weeks at room temperature.

Phthalyl bromide on exposure to air is readily converted into phthalic anhydride. A solution of phthalyl bromide in benzene, when mixed with excess of concentrated ammonia solution and kept over-night at room temperature, gives on acidification a large yield of *o*-cyanobenzoic acid, which without further crystallisation melts at 183—185° and is thereby converted into phthalimide. Similarly phthalyl bromide on warming with aniline in benzene during an hour gives an almost quantitative yield of phthalyldianilide, m. p. 253—255° after washing with benzene, alcohol, and water.

The treatment of phthalyl bromide immediately preceding the reaction with aniline causes great variation in the rate of this reaction. An almost saturated solution of phthalyl bromide in toluene (solution A) made in the cold and kept cold, gives merely a faint cloud with excess of aniline in toluene (solution B) during the first 15 seconds, and quite a slight precipitate in 60 seconds, although the precipitate becomes very copious in the course of a few minutes. Solution A, at any rate during the first minute of reaction when mixed with solution B, gives a smaller precipitate than does an equimolecular proportion of phthalic anhydride under the same conditions.

When solution A is heated in a sealed tube at 100° for 2 hours, and then rapidly cooled to room temperature, it fumes much more than before heating. Moreover, such a rapidly cooled solution, when poured into solution B, gives a much larger precipitate than was formed without the previous heating. The method does not lend itself to refined quantitative comparison, owing to the rate of filtration, and consequently the time of reaction in the two Gooch crucibles, being subject to great variation in the two cases. The point at issue has been proved in a number of experiments; *e.g.*, when the time of cooling the heated solution A to room temperature is 3 minutes, the ratio of the weights of the precipitates produced by comparable amounts of previously heated, and always cold solutions are about 50 in a reaction period of 15 seconds, and 5 in a reaction period of 60 seconds.

Solution A with the product obtained from carbon disulphide and piperidine in ether (von Braun, *loc. cit.*) gives a faint yellow. Solution A, heated and cooled, gives a deeper yellow, but in both cases the colour disappears in half an hour. The method Pfeiffer (*loc. cit.*) uses to discriminate between the two forms of phthalyl chloride fails with phthalyl bromide when acenaphthene or guaiacol is used.

A concentrated solution of phthalyl bromide in toluene, when made in the cold, has a green colour which slowly disappears on heating. The change, if any, which occurs in a cold solution in toluene has not yet been closely studied.

Preparation and Purification of Reagents for Rate of Reaction Measurements.—Benzoyl chloride, corr. b. p. 196·2—196·5°/761·3 mm., and benzoyl bromide, corr. b. p. 218—219°/761·7 mm., analytically pure, are obtained by fractionation of Kahlbaum's reagents. *Terephthalyl bromide* is made practically quantitatively by exposing the chloride (m. p. 81°) to a stream of dry hydrogen bromide at 150—160° for 30 hours. It is purified by distillation and crystallisation from petroleum (b. p. 80—100°), from which it separates in large prisms., m. p. 84—85°. After being kept in a sealed tube for a few months, the colourless crystals turn brown on the surface in a few minutes when the tube is opened, as though some slight decomposition had occurred (Found: Br, 54·9; hydrolysis value, 7·56 c.c. $C_8H_4O_2Br_2$ requires Br, 54·75%; hydrolysis value, 7·61 c.c.). Reference is made to the previous paper on phthalyl fluoride for particulars of the purification and preparation of other acid halides used. The small quantity of phthalic anhydride present in the phthalyl bromide and acyclic phthalyl chloride used was estimated by means of their hydrolysis value and halogen content, and is allowed for in weighing out the materials for reaction velocity measurements.

Rates of Reaction of iso*Propyl Alcohol with Phthalyl Bromide and Related Compounds.*—The procedure adopted is that described in connexion with phthalyl fluoride (*loc. cit.*). The concentration in all cases is 1/12·5 g.-atom of halogen per 1000 g. of *iso*propyl alcohol, and the temperature is 30·0°. The velocity constants recorded are determined from the unimolecular reaction $k = 1/t.\ \log_{10} a/(a - x)$, where t is measured in minutes.

k for benzoyl fluoride is $5{\cdot}1 \times 10^{-6}$, for benzoyl chloride (see Fig., curve 2) $2{\cdot}64 \times 10^{-3}$, and for benzoyl bromide $2{\cdot}43 \times 10^{-1}$, *i.e.*, the bromide reacts about 90 times faster than the chloride. Now, if phthalyl bromide has the same type of structure (II) as acyclic chloride, a roughly similar ratio is to be expected between their reaction rates with *iso*propyl alcohol. k for phthalyl bromide is $1{\cdot}6 \times 10^{-3}$, and for acyclic phthalyl chloride $0{\cdot}93 \times 10^{-2}$,* *i.e.*, the chloride is about 6 times more reactive than the bromide (see Fig., curves 3 and 1 respectively). This complete reversal of the order of activity indicates that the halides are of different types, *i.e.*, the bromide is cyclic. Further, making the assumption that the ratio of the reaction constants for the benzoyl and

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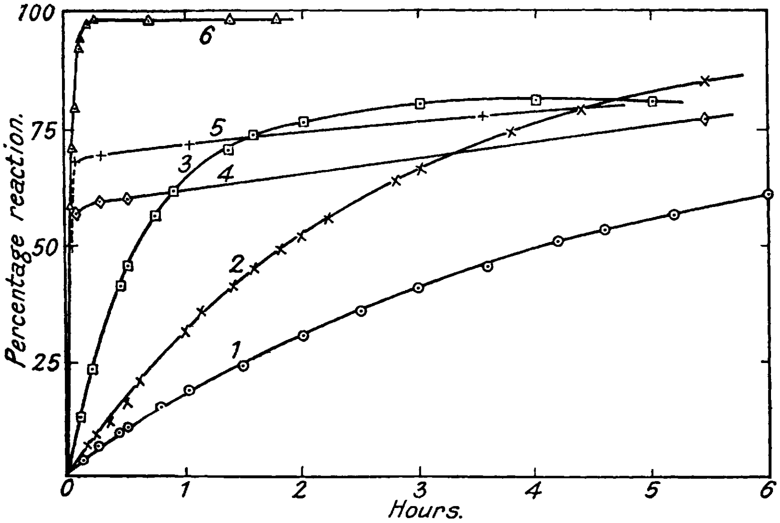
* The value $9{\cdot}93 \times 10^{-2}$ given for this constant (Dann, *et alii*, *loc. cit.*, p. 19) is a misprint for the above value $0{\cdot}93 \times 10^{-2}$.

phthalyl halides are strictly applicable, *k* for phthalyl bromide is 1/90 × 6 or 0·00185 of that expected if phthalyl bromide is acyclic. This compares closely with the ratio * (0·00179) of the reactivity of cyclic to acyclic phthalyl chloride.

The curve (6) for benzoyl bromide overlaps that for terephthalyl bromide, and as over 90% of the reaction in each case is complete in less than 5 minutes, it is impossible to determine *k* or the curve accurately. The great contrast between the curves (1) and (6) makes it very improbable that phthalyl bromide has the ·COBr form.

The Conversion of Phthalyl Bromide into a More Reactive Liquid Form.—A specimen of the above investigated phthalyl bromide is weighed into a thin-walled glass tube, which is then sealed, immersed in boiling water for 30 minutes, dried by wiping, and kept in a desiccator at room temperature for 20 minutes. The tube, in which the bromide is still liquid, is then broken in a flask containing sufficient *iso*propyl alcohol at 30° to make the solution contain 1/12·5 g.-atom of bromine per 1000 g. of alcohol. Samples are withdrawn for titration in the usual manner, and the curve (5) for liquid phthalyl bromide A obtained. Curve (4) for liquid phthalyl bromide B is obtained in exactly the same way, with the difference that the bromide, after being heated for 30 minutes, is kept at room temperature for 2 hours instead of 20 minutes.



Reaction curves : (1) *Phthalyl bromide,* (2) *benzoyl chloride,* (3) *acyclic phthalyl chloride,* (4) *liquid phthalyl bromide B,* (5) *liquid phthalyl bromide A,* (6) *benzoyl bromide (almost identical with that for terephthalyl bromide). All with* iso*propyl alcohol at* 30°.

The curves show that the previous action of heat greatly increases the activity of the bromide. The speed of reaction is so great that, as with terephthalyl bromide (6), no points can be obtained on the curves (5 and 4) for " activated " phthalyl bromide until more than 50% of the reaction is completed. Consequently the curve for the first part of the reaction cannot be exactly ascertained.

The change from inactive solid phthalyl bromide to active liquid phthalyl bromide is spontaneously reversible on cooling to the ordinary temperature. Curves (5) and (4) show that the " activated " phthalyl bromide loses its activity the longer it is cooled. The complete reversal is shown by the liquid phthalyl bromide solidifying at the ordinary temperature (in times varying from a few hours to several weeks) to form crystalline phthalyl bromide, which is identical in reactivity, m. p., and appearance with the original material. All the solid phthalyl bromide used in this investigation had not only been liquefied but distilled, and consequently must have been converted into the more reactive form. The product obtained by distillation, even at

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* This ratio is obtained as follows: Since at 30° phthalyl fluoride with methyl alcohol gives k_1 $5{\cdot}2 \times 10^{-3}$, and with *iso*propyl alcohol k_2 $5{\cdot}2 \times 10^{-5}$; and since cyclic phthalyl chloride with methyl alcohol gives k_3 $1{\cdot}7 \times 10^{-3}$, and acyclic phthalyl chloride with *iso*propyl alcohol gives k_4 $0{\cdot}93 \times 10^{-2}$; then, on obvious and probable assumptions, the desired ratio of the activity constants of cyclic to acyclic phthalyl chloride with methyl alcohol at 30° is k_3k_2/k_4k_1, that is, 0·00179.

temperatures as high as 200°, generally forms crystalline phthalyl bromide much more quickly than solid phthalyl bromide which has been reconverted into the active form by heating to 100° only. The sluggishness of crystallisation of phthalyl bromide is in marked contrast to the behaviour of terephthalyl bromide.

Determination of the Parachor of Phthalyl Bromide.—The experiments are carried out in the way previously described for phthalyl fluoride. The middle part of a large fraction of phthalyl bromide is taken and maintained solid at the ordinary temperature for several weeks, and the density and parachor determinations are made at 90°, *i.e.*, under conditions which allow transformation of the bromide. The density is difficult to determine without a trace of phthalic anhydride being formed.

Temp.	*H*, cm.	Cell const. $\times 10^{-3}$.	γ, dynes/cm.	*D*.	[*P*] found.	[*P*] calc.
90°	6·183	7·337	39·53	1·809	405·2	390·2 for (I)
90	6·227	7·307	39·64	1·807	405·3	404·9 for (II)

The gauge factor is 838·8.

These figures show that on melting and heating to 90° phthalyl bromide has the acyclic form (II).

Attempt to prepare Phthalyl Iodide.—A regular stream of hydrogen iodide is made by dropping a solution of iodine on red phosphorus, and the gas dried by passage over red phosphorus and then calcium iodide. When dry hydrogen iodide is passed into acyclic phthalyl chloride at room temperature or at 0°, the liquid immediately becomes brown, and after 15—30 minutes violent decomposition occurs with the evolution of iodine vapour and much heat.

SUMMARY.

Crystalline phthalyl bromide has been made in two ways, and a study of its rates of reaction with *iso*propyl alcohol shows it to have the cyclic formula. When melted and heated to 90°, phthalyl bromide exists as the acyclic compound, as is shown by parachor determinations and the rate of reaction with *iso*propyl alcohol and aniline. The two forms are tautomeric.

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