95. *Evidence for the Homolytic Bond Fission of "Positive Halogen" Compounds.*

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Catalysis of the autoxidation of tetralin provides evidence for the homolysis of many types of "positive halogen" compounds to free neutral radicals. Halogen compounds, such as *N*-chloroamides, which liberate iodine immediately from hydrogen iodide are immediate catalysts of the autoxidation of tetralin, and consequently are considered to decompose thermally to free halogen atoms and free organic radicals, both of which are active dehydrogenating agents. With many less active compounds the catalysis is more evident after an induction period, and in this case a second peroxide-catalysed chain reaction is thought to be involved.

The direct action between tetralin and certain of these halogen compounds has been studied, under nitrogen, and the results substantiate the theory of homolysis of the active halide and subsequent dehydrogenation of tetralin by the resulting active radicals.

" POSITIVE halogen " compounds, *e.g.*, types (I)—(V), which are characterised experimentally by liberation of iodine from hydriodic acid (1), are so called because they can be represented as acting by heterolytic bond fission to give halogen cations, rather than halogen anions, as in (2);

$\mathrm{Ar{\cdot}NCl{\cdot}COR}$ (I.) $\mathrm{CH_2Cl{\cdot}COR}$ (II.) $\mathrm{CR_1R_2Cl{\cdot}NO_2}$ (III.) $\mathrm{Ph{\cdot}CHBr{\cdot}CN}$ (IV.)

$$\mathrm{CH(CO_2Et)_2Br + 2HI \longrightarrow CH_2(CO_2Et)_2 + I_2 + HBr} \quad . \; . \; . \; . \; . \quad (1)$$

$$\mathrm{CH(CO_2Et)_2Br \longrightarrow \bar{C}H(CO_2Et)_2 + Br^+} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$
$$\mathrm{Br^+ + 2I^- \longrightarrow Br^- + I_2}$$

but whilst it can be shown that the organic radicals which promote reactions of type (1) are invariably groups of strong electron-attracting power, which must markedly diminish the normal tendency for a covalent halogen compound to split, on activation, to yield a stable halogen anion, yet it does not necessarily follow that bond fission of the converse type (*e.g.*, 2) is the only possible alternative. Indeed, theoretical calculations (compare Waters, *J.*, **1933**, 1551; **1942**, 153) show that in several typical " positive halogen " compounds, the inductive and mesomeric effects of the essential organic substituents do little more than *neutralise* the incipient polarisation of $\mathrm{C^-}$Halogen, or $\mathrm{N^-}$Halogen links, and hence a homolytic type of bond

$$\mathrm{CR_1R_2R_3{-}Hal \longrightarrow {\cdot}CR_1R_2R_3 + {\cdot}Hal} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

fission (3), giving rise to a neutral organic radical and an uncharged halogen atom, may well, in these compounds, require considerably less activation energy than any heterolytic dissociation.

Although the stoicheiometry of reactions involving " positive halogen " compounds does not allow one to discriminate between the heterolytic and the homolytic mechanism of bond fission, certain of their reactions, particularly in solvents of low ionising power, are indicative of the presence of free halogen atoms. Thus (*a*) *N*-chloroamides (I), like diazonium chlorides, readily react with metals such as mercury in several anhydrous solvents (Waters, *J.*, **1937**, 2011); (*b*) α-halogenated ketones (II) can, like organic peroxides, catalyse the " abnormal " addition of hydrogen bromide to olefins (Rust and Vaughan, *J. Org. Chem.*, 1942, **7**, 491); and (*c*) *N*-halogeno-amides (I) can substitute olefinic compounds in the α-methylenic position (Ziegler *et al.*, *Annalen*, 1942, **551**, 80) in a manner characteristic of the free neutral radicals or of molecular oxygen (compare Bloomfield, *J.*, **1944**, 114: Waters, *Nature*, 1944, **154**, 772).

Though the characteristic reactions of the " positive halogen " compounds can be depicted as processes of homolytic type, it does not necessarily follow from experimental evidence hitherto presented that they all actually do involve the disruption of an organic molecule and the liberation of *free* radicals. Very many organic reactions have proved to be solvolytic processes, or bimolecular reactions, in which bond fission, and any consequent electron transference, occurs without the separation of any " free " radical or ion, and there is no *a priori* method of computation which will decide whether or not a homolytic bond fission requires less activation energy than a bimolecular or multimolecular reaction. Some diagnostic experimental evidence for the occurrence of complete homolytic bond fission with certain " positive halogen " compounds is, however, presented below.

Catalysis of the chain reaction between tetralin and oxygen, which may be summarised by equations (4)—(6), has already been used by us (*Trans. Faraday Soc.*, 1946, **42**, 201; Waters, *ibid.*, p. 184; *J.*, **1946**, 1151) as evidence for the production of *free* radicals by dehydrogenation :

$$\mathrm{X{\cdot} + C_{10}H_{12} \longrightarrow X{-}H + {\cdot}C_{10}H_{11}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$
$$\mathrm{{\cdot}C_{10}H_{11} + O_2 \longrightarrow C_{10}H_{11}{-}O{-}O{\cdot}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$
$$\mathrm{C_{10}H_{11}{-}O{-}O{\cdot} + C_{10}H_{12} \longrightarrow C_{10}H_{11}{-}O{-}O{-}H + C_{10}H_{11}{\cdot}} \quad . \; . \; . \; . \; . \quad (6)$$

and since it has been abundantly shown (compare Waters, " The Chemistry of Free Radicals ", Oxford, 1946) that both free halogen atoms and free hydrocarbon radicals are hydrogen abstractors, as depicted by X· of equation (4), it follows that catalysis of the autoxidation of tetralin by positive halogen compounds affords a more conclusive proof of homolytic bond fission of the latter than does the occurrence of reactions of types (*a*) to (*c*) above.

TABLE I.

Catalysis of the autoxidation of tetralin by N-*halogeno-amides and -imides.*

Rate of oxygen uptake (ml. per 15 mins. per 25 ml. of tetralin).

	Time from start of autoxidation, mins.			
Compound (1 g. added).	0—15.	15—30.	45—60.	105—120.
Tetralin (reference blank)	1	1	1·6	2·0
N : 2 : 4-Trichlorobenzanilide	21	23	23	20
N : 2 : 4 : 6-Tetrachlorobenzanilide	15	19	18	15
N-Bromosuccinimide	11	12	11	6
Bis-*N* : 2 : 4 : 6-tetrachlorocarbanilide	9	11	3	—
N-Bromophthalimide	5	3	1	—
N-Chloroacetanilide	1	2	2	2·5
N : 2 : 4 : 6-Tetrachloroacetanilide	1	2	2	—

TABLE II.

Catalysis of the autoxidation of tetralin by " positive " C-*halogen compounds.*

Rate of oxygen uptake (as for Table I).

	Time from start of autoxidation, mins.			
Compound.	0—15.	15—30.	45—60.	105—120.
Ethyl α-bromomalonate	21	19	15	11
Chloropicrin	14	20	19	14
α-Bromobenzyl cyanide	15	14	12	10
p-Phenylphenacyl chloride	9	15	13	—
Bromonitroform	14	13	7	6
Chloroacetone	3	8	14	14
1-Chloro-1-nitropropane	2	4	7	10
ω-Tribromoquinaldine	3	6	10	11
Chlorotrinitromethane	5	5	5	3
α-Bromophenylacetamide	2	5	8	7
ω-Chloro-*p*-nitroacetophenone	2	3	4	5
Phenyl chloromethyl sulphone	2	3	3	—
2-Chloro-2-nitropropane	1·0	1·0	1·0	—
s-Dichloroacetone	1·0	1·0	1·0	—
(Comparison substances.)				
Ethyl malonate	1·0	1·0	1·0	—
Ethyl phenylacetate	1·0	2·0	2·0	—

TABLE III.

Alkyl, acyl, and aryl halides.

Rate of oxygen uptake (as for Table I).

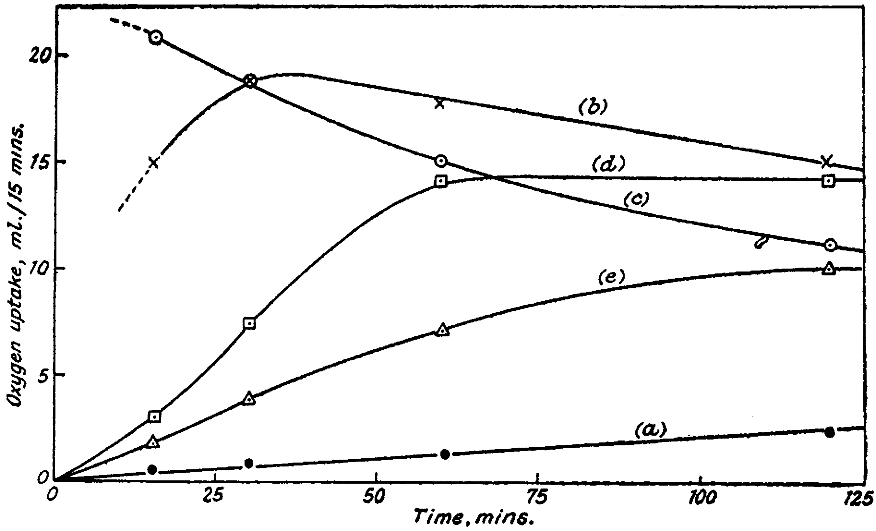
	Time from start of autoxidation, mins.			
Compound.	0—15.	15—30.	45—60.	105—120.
Benzyl bromide	9	15	17	14
Benzyl chloride	3	6	7	11
Ethyl bromoacetate	11	14	12	11
Ethyl dichloroacetate	1	4	12	14
Triphenylmethyl chloride	2	2	3	—
*cyclo*Hexyl chloride	2	3	3	—
α-Chloronaphthalene	3	3	4	—
Chlorobenzene	2	2	2	—
Benzoyl chloride	1	1	1	—
Ethyl chloroacetate	1	1	1	—
Hexachloroethane	2	3	3	—

The experimental results (*see* Tables I—III) show that " positive halogen " compounds of the widely varying types (I)—(V) do all act as immediate catalysts for the autoxidation of tetralin at 76°, and resemble therefore substances like dibenzoyl peroxide and benzene diazoacetate. Typical data are more clearly illustrated by the figure, in which, to show the salient features of this catalysis the *rate* of oxygen uptake by tetralin has been plotted against time.

Although freshly distilled tetralin has an exceedingly small initial rate of oxygen uptake, which slowly increases during a prolonged " induction period " (curve *a*) even when no special precautions have been taken to remove traces of adventitious catalysts, yet the addition of 3—4% of an *active* chlorinating agent, such as *N* : 2 : 4 : 6-tetrachlorobenzanilide (type I), immediately brings about oxygen absorption at a high rate (curve *b*). This high autoxidation rate is maintained for a long period, but eventually declines somewhat, probably because the homolytic dissociation of the *N*-halogen compound (reaction 3) produces progressively fewer and fewer chain-starting active fragments (X• of equation 4) as time goes on, and, in this capacity, is not adequately replaced by tetralin hydroperoxide, which is the main chain-starting agent concerned in the autoxidation of tetralin once the induction period is over (Robertson and Waters, *loc. cit.*).

Substances like ethyl α-bromomalonate (V) (which gave curve *c*), chloropicrin (III; $R_1 = R_2 = Cl$), and α-bromobenzyl cyanide (IV), which react very rapidly with potassium iodide in acetic acid, are also of this type. Corresponding halogen-free compounds, *e.g.*, ethyl malonate, were found to be quite inactive.

In contrast to these highly reactive substances, a number of halogen compounds which react slowly, if at all, with acidified potassium iodide give curves of the general type (*d*), in which the rate of oxygen uptake by tetralin, though always considerably greater than that of the untreated hydrocarbon, at first increases with time. Compounds such as chloroacetone (II; R = Me) (curve *d*), 1-chloro-1-nitropropane (curve *e*), benzyl bromide, and benzyl chloride, are of this type. This action is just that to be expected of a substance which undergoes homolysis (equation 3) very slowly, for then the enhanced rate of autoxidation could be due to the added effect of the accumulating tetralin hydroperoxide.



It would, however, be an over-simplification to consider only unimolecular dissociations of halogen compounds. Whilst the homolysis of many halides, such as benzyl bromide, may be more facile than their heterolysis in non-ionising solvents of low dielectric constant (compare Waters, *J.*, 1942, 153) such as tetralin, a unimolecular dissociation, *e.g.*, (7), is not the only

$$C_6H_5{\cdot}CH_2{\cdot}Br + \text{Energy} \longrightarrow C_6H_5{\cdot}CH_2{\cdot} + Br{\cdot} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

process which could decompose them to free radicals. A trace of any other radical-producing catalyst might first abstract a halogen atom (equation 8) whereupon there could be formed an

$$X{\cdot} + C_6H_5{\cdot}CH_2{\cdot}Br \longrightarrow X{\cdot}Br + C_6H_5{\cdot}CH_2{\cdot} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

active *free* hydrocarbon radical, capable of initiating the chain process (9) and (10) in which

$$C_6H_5{\cdot}CH_2{\cdot} + C_{10}H_{12} \longrightarrow C_6H_5{\cdot}CH_2\text{–}H + {\cdot}C_{10}H_{11} \quad . \; . \; . \; . \; . \quad (9)$$

$${\cdot}C_{10}H_{11} + C_6H_5{\cdot}CH_2Br \longrightarrow C_{10}H_{11}Br + C_6H_5{\cdot}CH_2{\cdot} \quad . \; . \; . \; . \quad (10)$$

free tetralyl radicals ($C_{10}H_{11}{\cdot}$) would participate, as well as in the concurrent autoxidation chain (5) and (6) which would thereupon occur. If reaction (8) is faster than (4) then the addition of a halide to tetralin will soon accelerate its autoxidation, although subsequently, if reaction (10) is much slower than (5), most of tetralin may be autoxidised and not brominated, and, on account of the occurrence of two competitive chain reactions, the autoxidation rate may never reach a particularly high value.

It must be noted that reaction (8), though bimolecular, still requires the homolysis of the halogen bond. Peroxide-catalysed addition and substitution reactions involve processes such as (8), and it may be suggested that with several of the less active halogen compounds cited in Tables I—III homolysis occurs, not by unimolecular dissociation (equation 3), but by reaction (8), in which the minute trace of tetralin hydroperoxide present in the tetralin used provides the radicals X• which act as a trigger to all the subsequent chemical changes. Support for this hypothesis is available elsewhere. Kharasch and Mayo (*J. Org. Chem.*, 1937, **2**, 76; *J. Amer. Chem. Soc.*, 1937, **59**, 1655), for instance, have shown that carbon tetraiodide and α-bromoacetoacetic ester, which are typical compounds of this group, are stable except in the presence of traces of oxygen, or of peroxides, whilst, more recently, Karrer and Schmid (*Helv. Chim. Acta*, 1946, **29**, 525) have shown that substitution in the α-methylenic position by means of *N*-bromosuccinimide is considerably accelerated by adding a little dibenzoyl peroxide to the reaction mixture.

To provide further evidence of the occurrence of reactions (9) and (10), certain of the reactions between tetralin and active halogen compounds have been studied in the absence of air. Tetralin, in carbon tetrachloride solution under a nitrogen atmosphere, reacts easily with *N* : 2 : 4-trichlorobenzanilide. Dichlorobenzanilide is precipitated, and the residual liquid, on careful fractionation, continually evolves hydrogen chloride, leaving 1 : 2-dihydronaphthalene, together with its polymer. When refluxed for some hours with tetralin under the same conditions, ethyl α-bromomalonate reacts slowly with evolution of hydrogen bromide. Ethy malonate could be isolated from the residual liquid, which also gave positive tests for both dihydronaphthalene and ethanetetracarboxylic ester. Reactions of dihydronaphthalene were also exhibited by the dark liquid obtained by prolonged refluxing of tetralin with benzyl bromide under nitrogen. Under these experimental conditions both tetralyl chloride and tetralyl bromide decompose to the corresponding halogen acid and 1 : 2-dihydronaphthalene (compare Bamberger, *Ber.*, 1890, **23**, 197).

Whilst the figures quoted in Tables I—III only give approximate relative values of reaction rates, they show very clearly the effect of structure on the ease of homolysis of both C–Halogen and N–Halogen bonds, and substantiate the form of the equation

$$E_{\text{Homolysis}} = E_{\text{Quantum forces}} + E_{\text{Coulombic forces}}$$

suggested previously (Waters, *loc. cit.*) for the activation energy of the changes involved. It will be seen that homolysis of C–Br is evidently more facile than that of C–Cl, and that substances which readily ionise ($E_{\text{Coulombic forces}}$ high), such as alkyl and acyl chlorides, have but little tendency to react homolytically.

EXPERIMENTAL.

Catalysis of the Autoxidation of Tetralin.—Autoxidation was studied in a 100-ml. "Pyrex" flask, fitted with a small tap-funnel, and a side tube leading, by a flexible joint, to a butyl phthalate manometer and a gas burette. The flask was shaken, at constant rate, in an oil-bath surrounded by a larger vessel of refluxing carbon tetrachloride, which kept the temperature steadily at 76°. For each test there were taken 25 ml. of tetralin which had been purified by fractionation up a column equivalent to 100 theoretical plates, and then had been redistilled at 15—20 mm. in a nitrogen atmosphere soon before use. Air was displaced from the system by evacuating at a water-pump and flushing several times with oxygen, drawn from a cylinder, and the initial rate of autoxidation of each batch of tetralin was first determined (this was always under 1 ml. per 15 min. and corresponded to a very slowly accelerating part of the "induction period", from which peroxide formation was just detectable). 1 G. of a solid halogen compound, or 1 ml. of a liquid, was then added, and after replacing air by oxygen, as before, the new rate of oxygen absorption was followed, at atmospheric pressure, for at least 2 hours. Tables I—III summarise averaged results, and indicate the order of the changes observed. They do not represent absolute measurements of reaction velocity.

Recently purified halogen compounds were used throughout. For instance, in the case of the benzyl chloride, to obviate the possible effect of catalysis due to a trace of benzaldehyde or its peroxide, the material was prepared from aldehyde-free (bisulphite washed) benzyl alcohol by the action of concentrated hydrochloric acid.

Reaction between Tetralin and N : 2 : 4 : 6-*Tetrachlorobenzanilide.*—0·1 Mol. of *N*-chloroamide, 0·5 mol. of tetralin, and 75 ml. of dry carbon tetrachloride were refluxed together for 2 hours under nitrogen. A small amount of hydrogen chloride was evolved. On removal of the carbon tetrachloride under reduced pressure trichlorobenzanilide separated in theoretical yield. The residual liquid was fractionated at 15 mm. pressure, giving fractions (*a*) b. p. 86°, consisting mainly of tetralin, (*b*) b. p. 120°, a liquid, from which however hydrogen chloride was evolved during the distillation, and (*c*) b. p. 220—230°, a viscous oil with a pronounced blue fluorescence in ultra-violet light.

Fraction (*a*), unlike pure tetralin, gave a blue colour on treatment with alcoholic sodium hydroxide, and immediately decolourised bromine in chloroform at 0°. After removal of chloroform from the brominated sample the residue, on storage at − 10°, deposited crystals of 1 : 2-dibromo-1 : 2 : 3 : 4-tetrahydronaphthalene, m. p. 73° after recrystallisation from alcohol (compare Hock and Susemihl, *Ber.*, 1933, **66**, 61).

Fraction (*b*) evolved hydrogen chloride at 190°, and the residue also gave the colour reaction and the bromine addition product characteristic of 1 : 2-dihydronaphthalene. Product (*c*) corresponds with the dimer of dihydronaphthalene described by Bamberger (*loc. cit.*) (Found: C, 91·7; H, 7·5. Calc. for $C_{20}H_{20}$: C, 92·3; H, 7·7%).

Fraction (*b*) presumably contains much 1-chloro-1 : 2 : 3 : 4-tetrahydronaphthalene, but attempts to characterise it more conclusively by hydrolysis to α-tetralol and preparation of its phenylurethane were not successful, since further fission to 1 : 2-dihydronaphthalene occurred on treatment with alkali.

N : 2 : 4-Trichlorobenzanilide reacted with tetralin in a similar manner.

Reaction between Tetralin and Benzyl Bromide.—0·1 Mol. of benzyl bromide, 0·5 mol. of tetralin, and 75 ml. of dry carbon tetrachloride were refluxed under nitrogen for 8 hours. The mixture gradually became yellow, and some hydrogen bromide was evolved (acid vapours; reaction with silver nitrate). On distillation at 15 mm. there were obtained (*a*) at 84—88° a mixture of tetralin and benzyl bromide, which gave positive tests for dihydronaphthalene, (*b*) at 140° a fraction which evolved hydrogen bromide during distillation, and which after further heating at 190° gave strong tests for dihydronaphthalene, and (*c*) a small quantity of the viscous polymer, of b. p. *ca.* 220°.

Reaction between Tetralin and Ethyl α-Bromomalonate.—This was carried out under the same conditions as the previous reaction. Fraction (*a*) gave tests for dihydronaphthalene. It was hydrolysed with hot aqueous alkali, and the aqueous solution thus obtained was concentrated, acidified, and treated with sulphuric acid and ethyl alcohol. About 2 g. of ethyl malonate, b. p. 195—198°, were thus obtained, and further characterised by preparation of crystalline malonamide. Fraction (*b*) again gave reactions of unstable bromotetrahydronaphthalene. The residue (*c*) again gave a water-soluble acid upon hydrolysis with alkali. This on treatment with resorcinol and sulphuric acid gave a fluorescein-like product, typical of succinic acid, and therefore may be considered to contain ethanetetracarboxylic acid. The quantity of acid isolated was, however, too small for effective purification.

A considerable amount of hydrogen bromide was evolved during the reaction between tetralin and the bromo-ester.

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