335. *Decomposition of DDT* [1 : 1 : 1-*Trichloro*-2 : 2-*di*-(4-*chlorophenyl*) *ethane*] *by Basic Substances.*

By K. A. Lord.

The reaction between DDT and some basic substances has been investigated at 30°. It has been shown that the rate of decomposition of DDT by methylamine is dependent upon the square of the amine concentration.

Consideration of the structure of DDT suggests that it will contain highly reactive chlorine atoms in the aliphatic part of the molecule, and the first recorded reaction of DDT is that of the elimination of hydrogen chloride from the molecule by alcoholic caustic alkali (Zeidler, *Ber.*, 1874, **7**, 1180). This reaction gives 1 : 1-dichloro-2 : 2-di-(4-chlorophenyl)ethylene, which is ineffective as an insecticide : it is therefore important to know the conditions under which it will occur, especially as it has formed the basis of a theory to account for the insecticidal activity of DDT (Martin and Wain, *Nature*, 1944, **154**, 512). In addition, at the time this work began, it seemed possible that DDT might form addition compounds with amines, and that this might account for its insecticidal activity. Preliminary experiments, however, showed that ammonia and simple amines decomposed DDT at room temperature to give the ethylenic compound. These reactions were therefore investigated more thoroughly. There was no evidence of the loss of further chlorine from the molecule, although other workers (Sheibley and Prutton, *J. Amer. Chem. Soc.*, 1940, **62**, 840; Cristol and Haller, *ibid.*, 1945, **67**, 2222; Martin and Wain, *Analyst*, 1947, **72**, 1) have described the removal of more chlorine than this from both DDT and its analogues.

Reaction of DDT with Amino-compounds.—The reactions between DDT, ammonia, and the methylamines in aqueous dioxan solution have been investigated. The reaction rate appears to run parallel with the amount of ionisation to be expected from the dissociation constants of the amines. It seems likely, therefore, that the reaction takes place between DDT and the amine ion, a conclusion borne out by the results with a series of other organic substances, some of which are of considerable biological importance, wherein it was found that only those which ionise to give an alkaline solution decompose DDT.

It can be shown that the reaction rate of DDT with both mono- and di-methylamine is proportional to the concentration of DDT. The reaction rate, however, depends on the *square* of the concentration of methylamine and is not directly proportional to it as might be expected from the investigations of Cristol (*J. Amer. Chem. Soc.*, 1945, **67**, 1494) on the decomposition of DDT by sodium hydroxide in alcoholic solution. This was confirmed by similar experiments with ethylene glycol monoethyl ether as solvent, showing the result not to be due to a specific solvent effect.

The dependence of the reaction rate on the square of the amine concentration can be explained by postulating either the formation of a DDT–amine complex or the reaction of DDT with a dimerised form of the amine.

The reaction between DDT and methylamine can be expressed stoicheiometrically by the equation

$$(C_6H_4Cl)_2CH{\cdot}CCl_3 + NH_2{\cdot}CH_3 \longrightarrow (C_6H_4Cl)_2C{:}CCl_2 + NH_2{\cdot}CH_3{,}HCl$$

and it has been shown experimentally that the rate of reaction $= k[\text{DDT}][NH_2{\cdot}CH_3]^2$.

The reaction taking place with the formation of a complex may be represented :

Stage I. $\text{DDT} + NH_2{\cdot}CH_3 \longrightarrow \text{Complex}$
Stage II. $\text{Complex} + NH_2{\cdot}CH_3 \longrightarrow (C_6H_4Cl)_2C{:}CCl_2 + NH_2{\cdot}CH_3{,}HCl + NH_2{\cdot}CH_3$

From stage I, $[\text{Complex}] \propto \dfrac{[\text{DDT}][\text{NH}_2\text{·CH}_3]}{k_1}$

From stage II, Rate of reaction $= k_2[\text{Complex}][\text{NH}_2\text{·CH}_3]$

Thus the rate of reaction $= k[\text{DDT}][\text{NH}_2\text{·CH}_3]^2$.

If reaction with the amine dimer is assumed, it can be shown that, if most of the amine is present as monomer, the dimer concentration is proportional to the square of the amine concentration, thus giving the equation for rate of reaction in accordance with experimental results. The arguments are applicable to the methylamine ion ($NH_3·CH_3^+$) as well as to the un-ionised amine. The reaction of DDT with an amine dimer seems unlikely under the conditions used.

Attempts to prepare compounds of various amines and DDT were not successful, and mixed melting-point curves of DDT with tribromoaniline, β-naphthylamine, benzamide, and acetanilide did not show compound formation; these results are in agreement with those of Martin and Wain (*loc. cit.*).

The reaction of carbon tetrachloride with simple aliphatic amines has recently been suggested to us as a possible model for this DDT decomposition.

Effect of Medium on Reaction Rate.—The reaction rate of DDT with aqueous sodium hydroxide is greatly affected by the reaction medium, the order of reaction with various DDT solvents being :

Ethylene glycol monoethyl ether > acetone > dioxan > benzene (= 0)

With alcoholic sodium hydroxide the reaction rates are in the same order but much higher, and the reaction rate in benzene is not zero. (Analogous effects are found with strong organic bases, *e.g.*, nicotine and methylamine.)

Catalytic Effect of Metals.—Catalysis of the thermal decomposition of DDT by metals or metallic oxides has been reported by a number of workers (Balaban and Sutcliffe, *Nature*, **1945**, **155**, 755; Fleck and Haller, *J. Amer. Chem. Soc.*, 1944, **66**, 2095). In the course of this work the decomposition of DDT by sodium hydroxide was shown to be catalysed by a number of metallic salts.

Effect of Degree of Alkalinity of Solutions.—It has been shown that, with all reagents in one phase, buffer solutions ranging from pH 7 to 11 decompose DDT, and in general the speed of reaction increases with increasing pH; some decomposition was noticeable at a pH as low as 7·1.

EXPERIMENTAL.

5 Ml. aliquots of DDT solution were measured into stoppered bottles at 30°; when thermal equilibrium had been attained 1 ml. portions of the appropriate reagent solution were added and the reaction allowed to proceed. The mixture was then acidified with 50% (8N) nitric acid, and excess of N/50-silver nitrate solution added, followed by 1 ml. of nitrobenzene and 5 drops of saturated ferric ammonium alum as indicator. The excess of silver was then titrated with ammonium thiocyanate (approx. N/50). When a substance such as nicotine, possessing an emulsifying effect, was present the precipitated silver chloride was filtered off before the titration. In a number of cases the results have been expressed as the fraction of DDT decomposed or the ratio of ionic chlorine found to the initial amount of DDT.

Order of Reaction of DDT with Methylamine.—The reaction of DDT with methylamine can be represented by the equation

$$(C_6H_4Cl)_2CH·CCl_3 + NH_2·CH_3 = (C_6H_4Cl)_2C{:}CCl_2 + NH_2·CH_3,HCl$$

If one reactant is in excess and the concentration of the other is c, the observed order of reaction n will be determined by the number of molecules of the reactant not in excess, and may be calculated by the differential method suggested by van't Hoff.

Thus $$-\,\mathrm{d}(c - x)/\mathrm{d}t = k(c - x)^n$$

and hence $$n \log (c - x) = \log k$$

which represents a straight line with slope n.

TABLE I.

2N-Ammonia (1 ml.) and 2N-DDT (5 ml.) in dioxan or benzene.

Time (days).	Cl′/DDT (dioxan).	Cl′/DDT (benzene).
0·0	0·00	0·00
1·75	0·05	0·00
3·72	0·10	0·00
5·78	0·14	0·00
7·81	0·16	0·00
9·83	0·17	0·02
12·80	0·25	0·02

TABLE II.

2N-Methylamine (1 ml.) and 2N-DDT (5 ml.) in dioxan.

Time (hours).	Cl'/DDT.	Time (hours).	Cl'/DDT.	Time (hours).	Cl'/DDT.	Time (hours).	Cl'/DDT.
0·00	0·00	9·50	0·28	23·58	0·51	51·13	0·71
1·67	0·06	11·25	0·31	26·83	0·54	63·25	0·79
3·25	0·11	13·83	0·35	31·00	0·55	72·00	0·81
5·08	0·17	16·00	0·40	40·50	0·66	87·83	0·86
7·50	0·22	20·67	0·46	43·50	0·64	92·75	0·89
						98·50	0·88

TABLE III.

2N-Dimethylamine (1 ml.) and 2N-DDT (5 ml.) in dioxan.

Time (hours).	Cl'/DDT.	Time (hours).	Cl'/DDT.	Time (hours).	Cl'/DDT.	Time (hours).	Cl'/DDT.
0·00	0·01	10·67	0·28	39·83	0·67	69·58	0·82
2·00	0·08	15·25	0·37	45·75	0·70	74·08	0·85
4·00	0·13	15·50	0·38	50·17	0·72	78·17	0·85
5·67	0·17	23·42	0·48	55·83	0·77	87·67	0·89
7·75	0·22	29·75	0·56	63·75	0·82	95·50	0·90

TABLE IV.

2N-Trimethylamine (1 ml.) and 2N-DDT (5 ml.) in dioxan or benzene.

Time (days).	Cl'/DDT (dioxan).	Time (days).	Cl'/DDT (dioxan).	Time (days).	Cl'/DDT (benzene).	Time (days).	Cl'/DDT (benzene).
0·00	0·00	7·00	0·24	0·0	0·00	5·0	0·02
0·13	0·00	9·00	0·22	1·0	0·01	8·0	0·03
2·00	0·07	12·00	0·25	2·0	0·00	11·0	0·04
4·08	0·12	15·13	0·28				

TABLE V.

0·44N-Methylamine (1 ml.) and 0·4N-DDT (5 ml.) in dioxan.

Initial concn. of DDT (*a*) = 0·333 g.-mol./l.
,, ,, methylamine (*b*) = 0·073 g.-mol./l.

Time (hours).	Concn. of Cl' (*x*).	Time (hours).	Concn. of Cl' (*x*).	Time (hours).	Concn. of Cl' (*x*).	Time (hours).	Concn. of Cl' (*x*).
0·00	0·000	16·08	0·023	54·17	0·047	87·50	0·051
2·50	0·005	18·50	0·023	64·00	0·046	92·08	0·052
3·00	0·006	21·75	0·027	64·20	0·047	94·42	0·053
4·92	0·008	30·08	0·033	69·50	0·051	96·00	0·054
8·25	0·015	40·10	0·039	81·00	0·052	112·00	0·055
		45·75	0·042			117·08	0·059

TABLE VI.

0·53N-Methylamine (1 ml.) and 0·10N-DDT (5 ml.) in dioxan.

Initial concn. of DDT (*a*) = 0·083 g.-mol./l.
,, ,, methylamine (*b*) = 0·088 g.-mol./l.

Time (hours).	Concn. of Cl' (*x*).	Time (hours).	Concn. of Cl' (*x*).	Time (hours).	Concn. of Cl' (*x*).	Time (hours).	Concn. of Cl' (*x*).
0·00	0·000	15·07	0·011	53·35	0·026	92·68	0·036
2·03	0·002	20·35	0·013	63·10	0·030	98·73	0·037
4·53	0·003	23·98	0·015	68·35	0·030	114·85	0·040
6·72	0·005	29·25	0·017	76·87	0·032	135·93	0·043
9·50	0·007	39·12	0·022	—	0·035	143·82	0·043
		44·37	0·023			149·73	0·046
		48·12	0·024				

TABLE VII.

0·53N-Methylamine (1 ml.) and 0·10N-DDT (5 ml.) in ethylene glycol monoethyl ether.

Initial concn. of DDT (*a*) = 0·083 g.-mol./l.
,, ,, methylamine (*b*) = 0·088 g.-mol./l.

Time (hours).	Concn. of Cl' (*x*).	Time (hours).	Concn. of Cl' (*x*).	Time (hours).	Concn. of Cl' (*x*).	Time (hours).	Concn. of Cl' (*x*).
0·00	0·000	5·85	0·011	18·08	0·023	52·22	0·040
2·00	0·005	11·28	0·017	25·55	0·028	71·35	0·042
3·40	0·007	12·33	0·018	34·65	0·031	72·25	0·043
3·43	0·007			47·73	0·040		

TABLE VIII.

0·53N-Methylamine (1 ml.) and 0·075N-DDT (5 ml.) in ethylene glycol monoethyl ether.

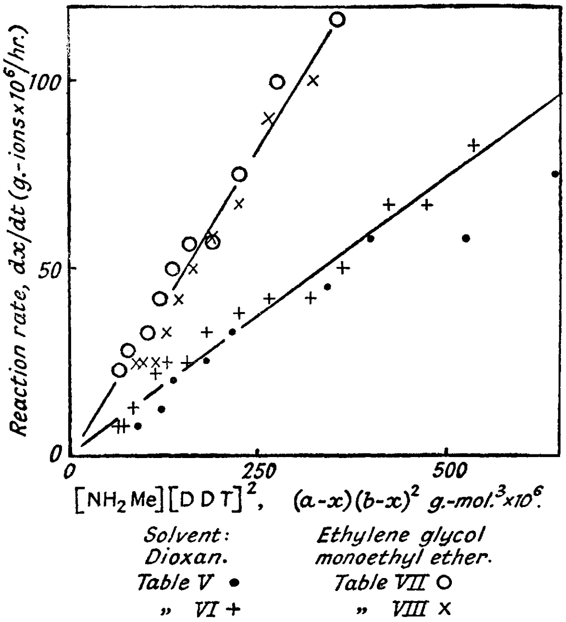
Time (hours).	Concn. of Cl′ (x).	Time (hours).	Concn. of Cl′ (x).	Time (hours).	Concn. of Cl′ (x).	Time (hours).	Concn. of Cl′ (x).
0·00	0·000	16·25	0·017	45·75	0·029	64·40	0·035
1·68	0·004	22·17	0·021	50·80	0·031	69·87	0·036
4·17	0·006	24·25	0·021	54·55	0·031	71·43	0·035
9·37	0·012	40·10	0·028	64·03	0·036	77·10	0·036

The reaction of DDT with methylamine in dioxan was followed with the amine in excess (Table II), and the reaction rate and concentration of DDT at various times determined. The order of reaction obtained by the method described above, log (reaction rate) being plotted against log (DDT concentration), was shown to be 1.

Similarly from the data in Table III it was shown that the reaction rate of dimethylamine with DDT is dependent upon the concentration of DDT.

The results in Table V show that the rate of reaction was dependent on the square of the free amine concentration.

Reaction of DDT with Methylamine.



Thus the rate of reaction of DDT with methylamine in water–dioxan (1 : 5) solution can be expressed by the equation

$$\text{Reaction rate} = dx/dt = k(a - x)(b - x)^2 = k[\text{DDT}][\text{amine}]^2.$$

Estimates of dx/dt plotted against those of $(a - x)(b - x)^2$ obtained from the data in Tables V and VI show a linear relationship and confirm this finding.

Similar estimates obtained from data on the reaction taking place in water–ethylene glycol monoethyl ether (1 : 5) (Tables VII and VIII) show that the same relationship holds in this medium (see figure).

Action of Various Substances on DDT Solutions at 30°.—A solution of DDT in ethylene glycol monoethyl ether was decomposed by aqueous solutions of sodium carbonate, guanidine carbonate, calcium hydroxide, and nicotine. Urea, glycine, lecithin, and creatinine had no apparent action. An aqueous solution of choline decomposed DDT in dioxan solution; sodium taurocholate and deoxycholate appeared to have a slight action, but not acetylcholine or ox bile.

Effect of Medium on the Decomposition of DDT in Solution by Sodium Hydroxide at 30°—The percentage decomposition caused by 1 ml. portions of aqueous sodium hydroxide added to 5 ml. of 0·10N-DDT in various solvents is summarised below.

Solvent.	Time (hours).	Percentage decomposition: 40% NaOH.	8% NaOH.
Benzene	25	1, 2	1, 1
Dioxan	20	4, 4, 3, 3	44, 46
Acetone	1	6, 7	32, 37, 37, 36
Ethylene glycol monoethyl ether...	1	92, 97	99, 98

The lower decomposition by 40% sodium hydroxide is probably due to the separation of the materials into two phases.

The action of 2N-alcoholic sodium hydroxide was almost complete in 1 minute in ethylene glycol monoethyl ether or acetone. The benzene solution showed 69—72% decomposition in 30 minutes. The decomposition of the dioxan solution after one minute was 34—47%, after two minutes 61—69%, after five minutes 93%, and after 30 minutes 100%.

Catalytic Effect of Metals.—0·1 Ml. of aqueous solutions of ferrous sulphate, ferric ammonium alum, copper sulphate, and manganese sulphate each containing 1% of metal, added to 5 ml. portions of 0·05N-DDT in acetone subsequently treated with 1 ml. of N-sodium hydroxide, caused increased decomposition. The percentage decomposition after one hour was: Fe$^{\cdot\cdot}$, 81; Fe$^{\cdot\cdot\cdot}$, 86; Cu, 86; Mn, 85; metal absent, 65.

A similar effect was observed in the case of an ethylene glycol monoethyl ether solution of DDT treated with nicotine. The percentage decomposition after 23 days in each case was: Fe$^{\cdot\cdot}$, 20; Fe$^{\cdot\cdot\cdot}$, 22; Cu$^{\cdot\cdot}$, 39; Mn, 9; Al$^{\cdot\cdot\cdot}$, 28; metal absent 14.

Effect of pH.—10 Ml. aliquots of N/50-DDT in ethylene glycol monoethyl ether were mixed with 2 ml. portions of buffer solutions shown below. The decomposition occurring was observed at various time intervals.

Buffer solutions.	pH.	Percentage decomposition. 7 days.	23 days.
4M/10-KH_2PO_4 + 3N/10-NaOH	7·1	2	12
4M/10-H_3PO_4 + 3N/10-NaOH	9·6	6	95
4M/10-$NaHCO_3$ + 3N/10-NaOH	10·0	19	92
4M/10-Na_2HPO_4 + 3N/10-NaOH	10·9	5	85
4M/10-$NaHCO_3$	8·0	12	56
4M/10-Na_2CO_3	10·2	28	100

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ROTHAMSTED EXPERIMENTAL STATION,
HARPENDEN, HERTS.

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