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Determination of p, p'-DDT in Commercial Samples

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A NUMBER of workers^{1,2,3,4} have employed dehydrohalogenation with boiling alcoholic alkali as the basis of a method for estimating $p_{,p'}$ -DDT. We have demonstrated,⁵ however, that at this temperature the reaction is not quantitative, slightly more than one equivalent of hydrogen chloride per molecule being released owing to the simultaneous formation of traces of bis-(p-chlorophenyl)-acetic acid. Nevertheless, at ordinary temperatures we found that decinormal alcoholic alkali removed hydrogen chloride quantitatively from p,p'-DDT, thus permitting exact determination of the substance. Such a procedure is not directly suitable for the estimation of the p,p' isomer in commercial samples owing to the presence of concomitant materials⁷ some of which also yield chloride ion under these conditions.⁸ The most important of these substances is o, p'-DDT, the dehydrohalogenation of which has been studied by Cristol.⁶ He showed that this isomer, which may occur in commercial samples to the extent of 8 to 21 per cent.,7 reacts with potassium hydroxide in 92.6 per cent. alcohol at 20.1° C. at only 1/67th the rate of the p,p' isomer. These results have led to the methods of Soloway et al.⁸ and of LaClair⁹ for the estimation of p,p'-DDT in commercial samples, in both of which methods the amount of chloride liberated under specified conditions is related to the content of p, p'-DDT by means of a regression equation.

The object of this paper is to present our information on the rates of dehydrohalogenation of o, p'-DDT, mixtures of this with the p, p' isomer, and commercial samples of DDT.

MATERIALS USED-

p,p'-DDT—The commercial material, crystallised three times from alcohol. Colourless needles, having m.p. 109° to 109.5° C.

o,p'-DDT—A sample kindly supplied by Dr. I. E. Balaban was recrystallised twice from methyl alcohol and gave colourless plates, m.p. 74° to 75° C., which did not depress the melting-point of an analysed specimen.

Commercial samples of $DD\hat{T}$ —Five samples, each representing an individual plant batch, were available. They were kindly provided by Dr. Balaban together with a statement of their p,p'-DDT content as determined by his crystallisation method.¹⁰

Absolute alcohol dried by standing over freshly ignited quicklime and fractionated, the fraction, b.p. 78° to 78.5° C., being collected.

Standard alcoholic potassium hydroxide solution—A.R. potassium hydroxide was heated under reflux with redistilled absolute alcohol and the solution was cooled, filtered and standardised. The concentration was 0.1964 N.

EXPERIMENTAL

(a) Rate of reaction of o,p'-DDT—500-mg. quantities of o,p'-DDT were weighed into separate 350-ml. conical flasks and dissolved in 25 ml. of absolute alcohol. Alternatively, 25-ml. aliquots, equivalent to 500 mg. of o,p'-DDT, of a standard solution in absolute alcohol were used. The flasks were stoppered and placed in a thermostat at 23°C. and after

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temperature equilibrium was attained 25 ml. of the standard alcoholic potassium hydroxide were added to each from a pipette. The final concentration of alkali was 0.0982 M and that of o, p'-DDT 0.0282 M. Each determination was performed in duplicate. The reaction was stopped after various times by addition of 25 ml. of N nitric acid and the liberated chloride then estimated by Volhard's method as previously described.⁵ The results are given in Table I.

TABLE I

Dehydrohalogenation of o, p'-ddt at 23° c.

Equivalents of Cl' liberated per molecule of DDT (average of duplicates)

mm.	
30	0.101
45	0.153
60	0.205
120	0.334
180	0.457

The equation for a bimolecular reaction may be expressed—

Time

$$K = \frac{2 \cdot 303}{t(b-a)} \log_{19} \left\{ \left(1 - \frac{ax}{b} \right) / (1-x) \right\}$$

where a is the initial concentration of o,p'-DDT, b is the concentration of potassium hydroxide, x is the fraction of DDT consumed in time t and K is the reaction constant.

Values of $\log_{10}\left\{\left(1-\frac{ax}{b}\right)/(1-x)\right\}$ were plotted against t and a straight line was obtained.

The reaction is thus bimolecular and under the conditions used, viz, employing absolute alcoholic potassium hydroxide at 23° C., the reaction constant K is 0.0008971 litres/mol./sec.

(b) Rate of reaction of p,p'-DDT—The rate of reaction of p,p'-DDT with alcoholic alkali under the same conditions was calculated from the results presented in our previous communication.⁵ This dehydrohalogenation was also found to be bimolecular, with a reaction constant of 0.03704 litres/mol./sec.

(c) Rate of reaction of mixed DDT isomers—Standard solutions in absolute alcohol were prepared containing p,p'- and o,p'-DDT in the respective ratios 90/10, 80/20 and 70/30 by weight. Of each solution, 25 ml. contained 500 mg. of the mixed isomers and this volume was allowed to react as before with 25 ml. of the standard alcoholic potassium hydroxide at 23° C. for various times. Liberated chloride was estimated in the usual manner. The results are presented in Table II. Curves expressing the rates of reaction of o,p' and p,p'-DDT and of the mixtures of these isomers with the standard alcoholic alkali are shown in Fig. 1.

TABLE II

Dehydrohalogenation of mixtures of p, p'- and o, p'-ddt at 23° c.

Equivalents of Cl' per gram molecule of total DDT

Time min.	90% p,p' + 10% o,p'	80% p,p' + 20% o,p'	70% p,p' + 30% o,p'	
15	0.857	0.764	0.670	
30	0.907	0.817	0.725	
60	0.922	0.840	0.754	
90	0.922	0.844	0.765	
120	0.935	0.869	0.785	
150	0.923	0.869	0.802	
180	0.949	0.887	0.826	

(d) Rate of reaction of commercial samples of DDT—5 g. of each sample, previously dried in vacuo, were accurately weighed and dissolved in absolute alcohol and the solution was diluted to 250 ml. Of each solution, 25-ml. aliquots were allowed to react for various times with equal volumes of the approximately 0.2 N alcoholic potassium hydroxide solution at 23° C. and the liberated chloride was estimated as before. The results are given in Table III, which also shows the percentage of p,p'-DDT in each sample as determined by the crystallisation method. The amount of chloride liberated cannot, of course, be expressed in this case as equivalents of Cl' per molecule of DDT, although the data in Table II can be readily

converted to mg. of Cl' per gram of DDT by multiplying by 100, the molecular weight of DDT being almost exactly ten times the atomic weight of chlorine.

TUDDD TIT	TABLE	III
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DEHYDROHALOGENATION OF COMMERCIAL DDT SAMPLES AT 23° C. Milligrams of Cl' liberated per gram of sample

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Time min.	Sample B (73.7% p,p')	Sample A (77.6% <i>p</i> , <i>p</i> ')	Sample E (80.8% p,p')	Sample D (82·8% p,p')	Sample C (89·2% p,p')
15	77.2	80.5	83.1	84.0	88.4
30	82.2	85.4	87.2	87.7	$92 \cdot 9$
60	84.5	87.1	89.1	89.6	94.1
90	85.7	88.3	89.7	90.2	94 ·5
120	87.0	89.3	90.7	90.9	94.8
180	88.6	90.7	91.8	92 ·0	95.3

DISCUSSION

The dehydrohalogenation of both o,p'- and p,p'-DDT, by means of absolute alcoholic potassium hydroxide at 23° C., has been shown to be a second-order reaction, the reaction constants being 0.0008971 and 0.03704 litres/mol./sec. respectively. These results may be compared with those of Cristol⁶ who, using 92.6 per cent. ethanol at 20.1° C., found both reactions to be of the second order with constants of 0.000371 and 0.02480 respectively. The effect of dilution of the solvent with water on the rate constant of the reaction was shown by Cristol to be consistent with electronic considerations.^{6,11} Thus by increasing the percentage of water in his aqueous alcohol solvent the rate constant for p,p'-DDT was decreased from 0.0248 for 92.6 per cent. alcohol to 0.0189 for 87 per cent. and to 0.0132 for 76 per cent. It is clear therefore that the present results with absolute alcohol are not inconsistent with those of Cristol, although under our conditions the ratio of the rates of dehydrohalogenation for the o,p' and p,p' isomers is only 1 : 41.3.

As would be expected, the rates of release of chloride ion from mixtures of the two pure isomers lie between those for p,p'- and o,p'-DDT (Fig. 1).







The five samples of commercial DDT, when dehydrohalogenated in absolute alcohol solution at 23° C., gave the results in Table III. Comparison of the data for sample C (89.2 per cent. of p,p') with that of the 90/10 mixture of the pure isomers shows that the technical DDT gives more chloride ion per unit weight, although the two materials have nearly the same content of p,p'-DDT. Moreover, as the p,p'-DDT content in the sample decreases, the discrepancy becomes greater owing to the enhanced interference of impurities (Fig. 3).

It is apparent, therefore, that unless a correction can be applied for chloride liberated from these extraneous materials, some empirical relationship must be sought between p,p'-DDT content and liberated chloride ion. Comparison of the rate constants of the two isomers shows that the reaction occurs rapidly with p,p'-DDT; we have observed that complete dehydrohalogenation (1 equivalent of Cl' per molecule) occurs within 60 minutes with this isomer, whereas, after the same interval, o,p'-DDT only loses 0.2 equivalents of Cl' per molecule. Since commercial samples contain more p,p'-DDT than any other constituent it was considered possible that the quantity of chloride ion liberated from a sample under our conditions would be proportional to the content of this substance. The percentage of p,p'-DDT in a commercial sample as determined by the crystallisation method was plotted



Fig. 3. Relation between p,p'-DDT content and chloride liberation in 60 minutes at 23°C.

against mg. of Cl' liberated per gram in 60 minutes' reaction time at 23° C. Good correlation was obtained, the curve within the limits investigated being linear (Fig. 3). The data for the mixtures of the pure isomers (Table II) also gave a straight line (Fig. 3), from which it is evident that the p, p'-DDT content of such a mixture can be accurately determined (cf. Soloway et al.⁸). It will be observed from Fig. 3 that the commercial sample line is higher than that obtained for the pure mixtures. It must be noted in this discussion that the ϕ, ϕ' -DDT contents of the commercial samples as obtained by the crystallisation method have been accepted, a point which may be open to objection as no method is yet available for the accurate determination of p, p'-DDT in the The commercial product. crystallisation figures, however, do afford a comparison between the different samples. It is also significant that the commercial sample line and that for the pure isomers, when extrapolated, meet at

a point corresponding approximately to 100 per cent. of p,p'-DDT. On the basis of these results the relationship between chloride liberated from a commercial sample under our conditions and its content of p,p'-DDT may be expressed as follows—

Percentage of p, p'-DDT = (1.56 × mg. of Cl' per gram of sample) - 58.1

This equation is given only tentatively, for in view of the fact that the proportion as well as the amount of the different impurities in separate batches of commercial DDT can vary, many samples would have to be critically examined before such an equation could be considered to be of general applicability. The results presented here, however, are in general agreement with those of LaClair,⁹ who also found a linear relationship between the chloride ion liberated from a series of commercial samples and their p,p'-DDT content as determined by a crystallisation method. The method of Soloway *et al.*⁸ for the estimation of p,p'-DDT in commercial samples, although similar, employs a regression equation that was calculated from the results of the decomposition of mixtures of the p,p' and o,p' isomers containing no other compounds. Our results confirm their findings, that such a procedure will tend to give high results with commercial samples owing to the liberation of chloride from other materials present.

SUMMARY

The dehydrohalogenations of o,p'- and of p,p'-DDT by means of absolute alcoholic potassium hydroxide at 23°C. have been shown to be second-order reactions with rate constants of 0.0008971 and 0.03704 litres/mol./sec. respectively. These results are in agreement with other published work, when differences in technique are taken into account.

The quantities of chloride ion released from mixtures of these isomers in various proportions and from commercial samples of DDT, on treatment with absolute alcoholic alkali at 23° C., have been determined. When these values were plotted against the p,p'-DDT content (determined in the commercial samples by a crystallisation method), straight lines were obtained which, when extrapolated, met at a point corresponding to 100 per cent. p,p'-DDT. A regression equation has been tentatively suggested; it should enable dehydrohalogenation of commercial samples under our conditions to give a close approximation to the p,p'-DDT content.

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DISCUSSION

Mr. D. E. BUTTERFIELD asked if the curve relating milligrams of chloride ion liberated to the percentage of p, p'-DDT was valid for various conditions of dehydrohalogenation or only for the conditions described by the authors. In reply, Dr. Wain stated that as the dehydrochlorination had not been investigated under other conditions it was impossible to give a precise answer to the question. La Clair, as already stated, had obtained similar results using mild conditions not greatly different from those employed in the present work. The use of more drastic alcoholic alkali treatment would be unsatisfactory owing to the occurrence of secondary reactions in which chloride ion becomes liberated.

Mr. L. G. UNSTEAD-JOSS asked if the nature of the substances present in commercial DDT that lose chlorine more rapidly than the p,p'-isomer with alcoholic alkali was known, and could they be removed to facilitate the determination? Dr. Wain reminded the speaker that commercial DDT was a very complex mixture. Certain constituents had been isolated which could yield more than one molecule of hydrochloric acid under specified conditions, but no method had been proposed whereby such substances could be removed prior to the estimation.

Dr. H. LIEBMANN asked what was the minimum quantity of DDT with which the described method could deal in the analysis of residues. Dr. Wain replied that in work on the estimation of pure p, p'-DDT residues on leaf tissues carried out at East Malling Research Station under his supervision, quantities as low as 200 mg. had been determined by the dehydrohalogenation method. The accurate estimation of residual deposits of commercial DDT on leaf tissue was complicated by the loss of various constituents during weathering and by penetration into the leaf tissue. These factors altered the composition of the deposit.

Dr. D. M. WRIGHT enquired about the extent of the danger to bees from fruit-blossom spraying with liquids containing DDT and whether earlier, pre-blossom spraying was preferable, so as to avoid the contact toxicity but retain the stomach toxicity to leaf-eating insects. Dr. Wain replied that whereas it was probably advisable to avoid spraying the open blossom with DDT preparations, recent work had shown that, at the concentrations normally used, this insecticide, even on open blossom, was practically harmless to foraging bees. Benzene hexachloride preparations, however, were decidedly toxic.

Dr. HAMENCE asked (1) if DDT was easily hydrolysed by water; if one had a few leaves to test would there be much risk of decomposition in extracting any residue with alcohol? (2) which of the colour reactions for DDT that have been recommended in the American literature did Dr. Wain consider the most useful? (3) in examining commercial DDT what did Dr. Wain consider a reasonable minimum content of the active isomer? Dr. Wain stated that DDT was not hydrolysed by water. Alcohol was not a good solvent for extracting the residual deposits from leaves as it did not dissolve DDT readily. In his own experiments with pure p, p'-DDT, Dr. Wain had obtained satisfactory results by washing the leaves with benzene. Such treatment, however, removed the surface deposit only; the insecticide that had penetrated the leaf tissue could be recovered only by Soxhlet extraction. Of the colour reactions for DDT, the speaker considered that of Schechter and Haller, involving nitration followed by treatment with sodium methoxide, to be the most satisfactory and selective for p, p'-DDT. Seventy per cent. was a reasonable minimum content of p, p'-DDT in a commercial sample.