after this evacuation show that the samples did not develop porosity and did not increase their surface areas during degassing.

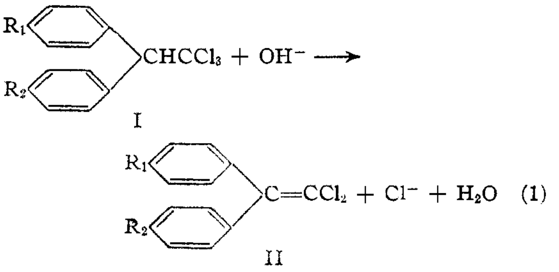
PITTSBURGH, PA. RECEIVED MAY 21, 1945

[CONTRIBUTION FROM THE BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, AGRICULTURAL RESEARCH ADMINISTRATION, U. S. DEPARTMENT OF AGRICULTURE]

A Kinetic Study of the Dehydrochlorination of Substituted 2,2-Diphenylchloroethanes Related to DDT[1]

BY STANLEY J. CRISTOL

Brand and Busse-Sundermann[2] have reported a semiquantitative kinetic study of the dehydrochlorination of several 2,2-diaryltrichloroethanes with potassium hydroxide in 96% ethanol at the boiling point of the solution. The reaction studied is represented by equation (1).



These workers, as well as Neal[3] and Gunther,[4] have demonstrated the quantitative nature of this reaction, and their work has indicated that only one mole of chloride ion is produced per mole of trichloroethane at 80°. Grummitt, Buck and Jenkins[5] have shown that at elevated temperatures hydrolysis of the ethylene (II, $R_1 = R_2 =$ Cl) may occur with the formation of a substituted diphenylacetic acid.

In connection with an extended study in our laboratory of the insecticide DDT (I, $R_1 = R_2 =$ Cl) and of analogs of DDT, a quantitative study of the effect of modifications in molecular structure upon chemical reactivity was undertaken. Alkaline dehydrochlorination was chosen as a suitable reaction, as its course may be conveniently followed by titration for chloride ion and the reaction forms the basis for an analytical method for the determination of DDT.[3,4] This reaction was also of interest in connection with work on the mode of action of DDT, since at least two groups of workers[6,7] have suggested the possibility that dehydrochlorination may be involved in the toxic action of DDT against insects.

The purpose of this paper is to report kinetic data on the elimination of hydrogen chloride with ethanolic sodium hydroxide from compounds of type I with R_1 = H and R_2 = H or Cl, and with $R_1 = R_2 =$ H, Cl, Br, F, CH_3, CH_3O or *t*-butyl, and of one series of related compounds in which the trichloromethyl group has been replaced with dichloro- and monochloromethyl groups. This work also includes data on the *o,p'*-DDT isomer, 1-trichloro-2-*o*-chlorophenyl-2-*p*-chlorophenylethane. Rate constants were obtained at 20.11 and 30.37° in 92.6 weight per cent. ethanol with all the compounds studied. The effect of change of solvent to 87.0 and 76.0 weight per cent. ethanol on the rate of dehydrochlorination of *p,p'*-DDT has also been studied.

Measurement of Reaction Rates.—The following procedure was used to follow the rates of reaction of the various chloroethanes with sodium hydroxide: A solution containing the ethane, 0.005 to 0.01 *M*, and sodium hydroxide, 0.01 to 0.05 *M*, was prepared at the desired reaction temperature by dissolving the required weight of the ethane in "190-proof" ethanol in a volumetric flask (adding the required amount of water in certain cases), equilibrating the solution in a thermostat, and then adding, by means of a pipet, a measured volume of standard ethanolic sodium hydroxide. The solution was then made up to volume, mixed well by shaking, and replaced in the thermostat at 20.11 or 30.37°. Temperature control was constant within ±0.03°. During the course of a run six or seven 10.00- or 20.00-ml. aliquot samples were transferred to an Erlenmeyer flask at bath temperature, and the reaction was then stopped by the addition of about 25 ml. of 1.5 *N* nitric acid. The solutions were then treated with 5.00 ml. of standard 0.03 *N* silver nitrate solution, and the precipitate was coagulated with nitrobenzene. The excess silver ion was titrated with standard 0.02 *N* ammonium thiocyanate with the use of a microburet and ferric sulfate as indicator in the customary Volhard procedure.

In extremely rapid reactions the temperature of the room was maintained within 1° of the bath temperature to minimize errors arising during the period of transfer, which was approximately one minute.

Sodium hydroxide was chosen as the basic re-

---

[1] This research was conducted under a transfer of funds, recommended by the Committee on Medical Research, from the Office of Scientific Research and Development to the Bureau of Entomology and Plant Quarantine. Not copyrighted.

[2] Brand and Busse-Sundermann, *Ber.*, **75**, 1819 (1942).

[3] Neal and co-workers, *U. S. Pub. Health Service*, Suppl. to Pub. Health Repts. No. 177 (1944).

[4] Gunther, *Ind. Eng. Chem., Anal. Ed.*, **17**, 149 (1945).

[5] Grummitt, Buck and Jenkins, THIS JOURNAL, **67**, 156 (1945).

[6] Fleck and Haller, *ibid.*, **66**, 2095 (1944).

[7] Martin and Wain, *Nature*, **154**, 512 (1944).

agent rather than potassium hydroxide because of the higher solubility of sodium chloride in ethanol.[8] The titer of the standard sodium hydroxide solution used was checked periodically against standard hydrochloric acid.

The solvent, commercial "190-proof" ethanol, was used without purification. It had a density (20/4° corrected to vacuum) of 0.8109, which is equivalent to 92.6 weight per cent.

Calculation of the Rate Constants.—The reaction given in equation (1) was found to be of the second order—that is, first order with respect to both chloroethane and hydroxide concentrations—and use was made of the following equation connecting initial ethane concentration a, initial hydroxide concentration b, fraction φ of ethane consumed, and time t:

$$\mathrm{d}\log\frac{1 - a\varphi/b}{1 - \varphi}\Big/\mathrm{d}t = \frac{b - a}{2.303}\,k \qquad (2)$$

Values of $\log (1 - a\,\varphi/b)/(1 - \varphi)$ corresponding to the various samples of a run were plotted as ordinates against corresponding values of time, t, and the best straight line was drawn by inspection through the points. The slope of this line was multiplied by the value of $2.303/(b - a)$ for the run to give the rate constant k. This method does not give undue weight to the first analysis made, nor is the value of k affected by uncertainties involved in the time taken as the start of reaction. A typical treatment of the data is shown in Fig. 1, which is the plot of two runs with p,p'-DDT at 20.11°. Satisfactory values were obtained with the second-order rate expression for all the compounds studied. Table I presents the data and results for all the experiments in 92.6% ethanol.

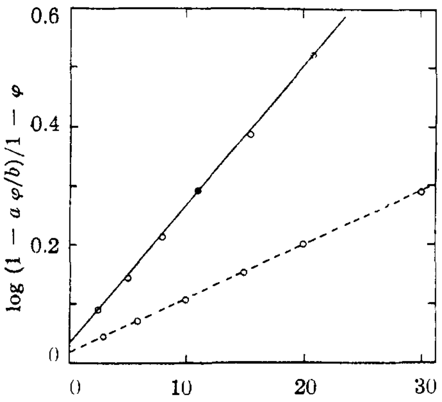


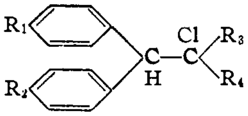
Fig. 1.—Treatment of data for rate constant of p,p'-DDT at 20.11°: O—O, DDT = 0.0100 M, NaOH = 0.0475 M; O----O, DDT = 0.0100 M, NaOH = 0.0238 M.

Medium Effects on the Rate Constants.—No salt effect was noted in studies with p,p'-DDT when the concentration of sodium hydroxide was varied from 0.012 to 0.048 M. This is in agreement with theory for a second-order reaction in which one of the reactants is a neutral molecule.

The effect of variation in solvent is shown in Table II. Although part of this change may be due to the change in the hydroxide–ethoxide equilibrium, the major change in rate is undoubtedly due to the effect of the greater ionizing power of the solvent upon k. The mechanism of the elimination process here involved is clearly that denoted by Hughes and Ingold[9] as E_2, and the decrease in k produced by increasing amounts of water is as predicted by them.

TABLE I

DATA AND RESULTS FOR REACTION RATE CONSTANTS AND HEATS OF ACTIVATION FOR DEHYDROCHLORINATION WITH SODIUM HYDROXIDE IN 92.6% ETHANOL OF COMPOUNDS



Substituent R₁	R₂	R₃	R₄	Temp., °C.	Halide a, M	NaOH b, M	Rate constant 10^5k, liters/sec./mole	Av.	Average deviation, %	Heat of activation, k cal.
Cl	Cl	Cl	Cl	20.11	0.00991	0.0472	2420	2480	2.5	18.2
					.00998	.0475	2440			
					.01001	.0238	2530			
					.01001	.0238	2390			
					.00501	.0119	2540			
					.00501	.0119	2560			
				30.37	.00495	.0118	6960	7110	2.1	
					.00497	.0118	7260			
Cl	[a]	Cl	Cl	20.11	.01006	.0476	36.4	37.1	1.9	20.4
					.01009	.0476	37.8			
				30.37	.01022	.0472	121	121	..	
					.01002	.0472	121			
Br	Br	Cl	Cl	20.11	.00503	.0238	3510	3470	1.2	18.8
					.00504	.0238	3430			
				30.37	.00478	.0118	10200	10300	1.0	
					.00478	.0118	10400			

---

[8] Ferner and Mellon, *Ind. Eng. Chem., Anal. Ed.*, **6**, 345 (1934).

[9] Hughes and Ingold, *Trans. Faraday Soc.*, **37**, 657 (1941).

TABLE I (*Concluded*)

	Substituent									
R_1	R_2	R_3	R_4	Temp., °C.	Halide a, M	NaOH b, M	Rate constant 10^5k, liters/sec./mole	Av.	Average deviation, %	Heat of activation, kcal.
F	F	Cl	Cl	20.11	.01009	.0476	305	303	0.8	19.5
					.01013	.0476	300			
				30.37	.01028	.0472	924	940	1.7	
					.01028	.0472	956			
H	Cl	Cl	Cl	20.11	.01004	.0475	298	301	0.8	19.0
					.01010	.0475	303			
				30.37	.01002	.0472	910	904	1.3	
					.01003	.0472	898			
H	H	Cl	Cl	20.11	.01051	.0475	36.8	36.9	0.4	21.3
					.01048	.0476	37.1			
					.01048	.0475	36.8			
				30.37	.01053	.0472	129	127	1.0	
					.01053	.0472	125			
					.01048	.0472	127			
					.01053	.0472	128			
CH_3	CH_3	Cl	Cl	20.11	.01003	.0475	10.9	10.9	..	21.0
					.01003	.0475	10.9			
				30.37	.01025	.0472	36.9	36.9	..	
					.01022	.0472	36.9			
t-Bu	*t*-Bu	Cl	Cl	20.11	.00502	.0474	10.9	10.7	1.9	19.8
					.00504	.0475	10.5			
				30.37	.00479	.0461	33.5	33.7	0.4	
					.00479	.0461	33.8			
CH_3O	CH_3O	Cl	Cl	20.11	.00912	.0476	9.18	9.18	..	20.6
					.00913	.0476	9.18			
				30.37	.00875	.0472	29.9	30.3	1.2	
					.00914	.0472	30.6			
Cl	Cl	Cl	H	20.11	.01007	.0476	568	567	0.2	19.1
					.01009	.0476	566			
				30.37	.00504	.0236	1720	1720	2.5	
					.01003	.0472	1660			
					.01005	.0472	1790			
Cl	Cl	H	H	20.11	.01050	.0475	91.6	91.0	0.7	19.5
					.01044	.0475	90.4			
				30.37	.01046	.0472	285	282	2.1	
					.01072	.0472	279			

[a] This compound, *o,p'*-DDT, has R_2 = H and a chloro substituent in the *ortho* position of this same ring.

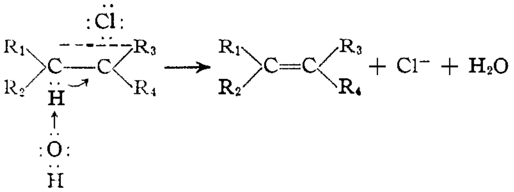
TABLE II

EFFECT OF SOLVENT UPON REACTION-RATE CONSTANT IN AQUEOUS ETHANOL FOR *p,p'*-DDT AT 20.11°

Ethanol, wt. %	*p,p'*-DDT, a, M	NaOH, b, M	Rate constant, 10^5k liters/sec./mole	Av.
92.6	.....	....	..	2480
87.0	0.01001	0.0238	1930	1890
	.01001	.0238	1850	
76.0	.00501	.0119	1340	1320
	.00501	.0119	1310	

Effect of Structure upon Reactivity.—The specific reaction-rate constants and Arrhenius heats of activation are given in Table I. Since the reaction-rate determinations were made at only two temperatures, the values for heat of activation must be considered as approximate.

The mechanism of the E_2-type elimination may be represented as follows



(3)

The speed of the reaction is therefore dependent upon the relative availability of electrons for the carbon–hydrogen bond undergoing rupture. This in turn is dependent upon the electron-attracting or electron-repelling properties of groups R_1, R_2, R_3, and R_4 in equation (3). The effect of substitution of electron-attracting groups in the series might then be predicted to produce an increase in k.

Such an effect was noted in a study of the series 1-chloro-2,2-bis-(p-chlorophenyl)-ethane, 1,1-dichloro-2,2-bis-(p-chlorophenyl)-ethane, and 1-trichloro-2,2-bis-(p-chlorophenyl)-ethane, where $R_1 = R_2 = p\text{-ClC}_6\text{H}_4$ and a change from $R_3 = R_4 = \text{H}$ to $R_3 = \text{Cl}$, $R_4 = \text{H}$ produced a six-fold increase in k and a change to $R_3 = R_4 = \text{Cl}$ produced a further four-fold increase.

In the other series studied—that is, the 1-trichlorodiarylethanes, where $R_3 = R_4 = \text{Cl}$ and R_1 and R_2 are phenyl or substituted phenyl groups—an attempt was made to correlate reactivity with substituent in the *para*-substituted compounds. Hammett[10] has shown that the rate and equilibrium constants of a large number of side-chain reactions of m- and p-substituted benzene derivatives may be satisfactorily correlated. He has accordingly set up a series of substituent constants σ, dependent only upon the nature and position of the substituent and a series of reaction constants ρ which are constant for all substituents and depend only upon the reaction series. These are interrelated by the equation

$$\log k - \log k_0 = \rho\sigma \qquad (4)$$

where k is the velocity or equilibrium constant of the reaction for the substituted organic reactant, and k_0 that for the unsubstituted organic reactant.

On the assumption that the substituent constants derived for substituted monophenyl derivatives may be used for substituted diphenyl derivatives—that is, that the effects reflected in σ are additive—log k for the dehydrochlorination reaction at 20.11° was plotted against the sum of Hammett's σ values for the individual substituents and the best straight line constructed. The results are indicated as the solid line in Fig. 2. The slope of the line ρ, and the intercept log k_0, calculated by the method of least squares, had the respective values 2.661 and −2.938. The probable error, r, of the measured log k values from those predicted from this relationship was calculated from Bessel's formula and was found to be 0.177.

It will be noted in Fig. 2 that the observed values for the diphenyl and chlorophenylphenyl derivatives have large negative deviations from the standard line. The dotted line in Fig. 2 represents the line of slope $\rho = 2.729$ and intercept log $k_0 = -2.822$, which has been obtained by the method of least squares from the di-p-substituted reactants, and the observed log k values for these compounds have a probable error r of only 0.110 from the calculated. These values of r, which should be halved for fair comparison with mono-aryl derivatives to values of 0.089 and 0.055, compare favorably with the mean value of probable error in log k of 0.060 found by Hammett for 52 reactions of mono-phenyl derivatives.

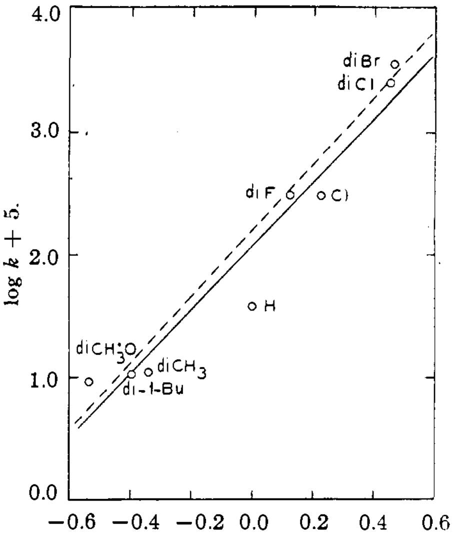


Fig. 2.—Relationship between log k of dehydrochlorination reaction and substituent constant: O—O, calcd. for all compounds; O----O, calcd. for disubstituted compounds only.

Further experimental justification for the conclusion that data on disubstituted diaryl derivatives may not be considered together with those on mono-substituted derivatives has been found in the work of Norris and co-workers[11,12] on the rates of reaction of substituted benzohydryl chlorides with ethanol at 25°. Their data for the first-order reaction rate constants have been recalculated on the basis of the second as unit of time, and the values have been plotted in Fig. 3 against corresponding values of σ. The linear

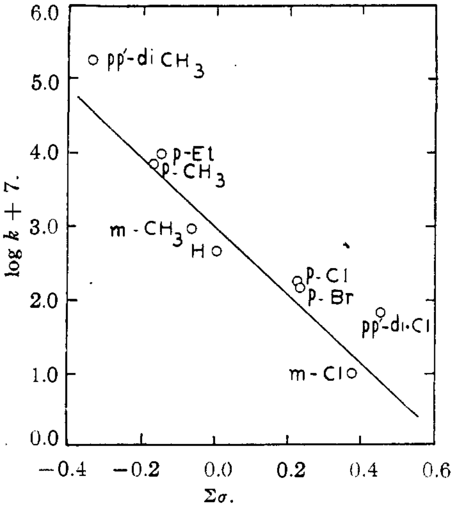


Fig. 3.—Relationship between log k for ethanolysis of substituted benzohydryl chlorides and substituent constant; data of Norris, Banta and Blake.[11,12]

---

[10] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter VII.

[11] Norris and Banta, THIS JOURNAL, **50**, 1804 (1928).

[12] Norris and Blake, *ibid.*, **50**, 1808 (1928).

relationship plotted was derived by the method of least squares using only the data for benzohydryl chloride and its mono-substituted derivatives. The calculated intercept, log k_0, was -4.014, and the slope, or reaction constant ρ, was -4.645. The probable error r obtained for the unsubstituted or monosubstituted compounds was found to be 0.205, whereas the deviation for the two disubstituted compounds was 0.789, both observed values being high.

Thus the limited data available would suggest that, although a fairly satisfactory correlation may be made of reaction constants of diaryl derivatives with the substituent constants derived from monoaryl compounds, there may be measurable differences between disubstituted and monosubstituted compounds. Another way of stating this is that the value of σ for hydrogen may not be zero for the second ring. This conclusion must be regarded as tentative pending further study.

Relative Rates for *o,p'*- and *p,p'*-DDT Isomers.—The relative rates of dehydrochlorination of *o,p'*- and *p,p'*-DDT isomers are of special interest, since these compounds are the major constituents in technical DDT.[13] The large value of the ratio of the rate constants at 20.1°, 0.0248/0.000371 = 66.9, suggests that a method for the analysis of technical DDT or of spray residues containing DDT for the *p,p'*-DDT isomer (which is the more active insecticidal agent) may be devised. Work is now in progress in this Laboratory toward that end. This method would have an advantage over the present dehydrochlorination analytical methods[3,4] in that these methods measure the total content of all isomers present, rather than that of the most active principle.[14]

Materials Used

1-Trichloro-2,2-bis-(*p*-chlorophenyl)-ethane (*p,p'*-DDT).—This compound was prepared by recrystallization from technical DDT[13] and melted at 108–109° (cor.).

1-Trichloro-2-*o*-chlorophenyl-2-*p*-chlorophenylethane (*o,p'*-DDT) was prepared from 2-trichloro-1-*o*-chlorophenylethanol and chlorobenzene[13] and melted at 74.0–74.5° (cor.).

1-Trichloro-2,2-bis-(*p*-bromophenyl)-ethane was prepared from chloral and bromobenzene[15] and melted at 142.9–143.6° (cor.).

1-Trichloro-2,2-bis-(*p*-fluorophenyl)-ethane.—This compound was kindly furnished by Capt. W. H. Rueggeberg, U. S. Army. It melted at 42–45° (cor.).

1-Trichloro-2-*p*-chlorophenyl-2-phenylethane,[6] **1-trichloro-2,2-diphenylethane**[16] and **1-trichloro-2,2-di-*p*-tolylethane**[17] were kindly furnished by Dr. E. E. Fleck. The compounds melted at 77.0–77.5, 64.0 64.2 and 88.2–89.0° (cor.), respectively.

1-Trichloro-2,2-di-*p*-anisylethane[18] was prepared by R. K. Preston and melted at 87–88° (cor.).

1-Trichloro-2,2-bis-(*p*-*t*-butylphenyl)-ethane[19] was prepared by R. A. Hayes from chloral and *t*-butylbenzene and melted at 154–155° (cor.).

1,1-Dichloro-2,2-bis-(*p*-chlorophenyl)-ethane[13] and **1-chloro-2,2-bis-(*p*-chlorophenyl)-ethane,**[20] were kindly furnished by Dr. P. D. Bartlett, of Harvard University. The compounds melted at 109.4–110.2° and 51–53° (cor.), respectively.

Summary

A kinetic study has been made of the dehydrochlorination with sodium hydroxide of eleven 2,2-diarylchloroethanes related to DDT. The reactions have been found to be of the second-order E_2 type. The effects of changes in solvent and of increase from chloromethyl to dichloromethyl and trichloromethyl in one group of compounds have been shown to be as predicted for the E_2 type.

The experimental values of reaction rate constants for eight diaryltrichloroethanes with para substituents were found to be in fair agreement with those predicted by the Hammett equation. The scale of the deviations suggests, however, that there may be necessary a slight difference in treatment of disubstituted-diaryl derivatives as compared with monosubstituted-diaryl derivatives. The work of Norris on the ethanolysis of diarylchloromethanes has been analyzed and shown to be in agreement with this conclusion.

The rate constant for the *o,p'*-DDT isomer, which is the principal impurity in technical DDT, has been shown to be $^{1}/_{67}$ that of the *p,p'*-DDT isomer, which is the principal insecticidal agent.

BELTSVILLE, MARYLAND RECEIVED JUNE 30, 1945

---

[13] Haller, Bartlett, Drake, Newman and co-workers, THIS JOURNAL, 1591 (1945).

[14] See Cristol, Hayes and Haller, *Ind Eng. Chem., Anal. Ed.*, **17**, 470, (1945), for further discussion and a description of a recrystallization analytical procedure for *p,p'*-DDT.

[15] Zeidler, *Ber.*, **7**, 1180 (1874).

[16] Baeyer, *ibid.*, **5**, 1098 (1872).

[17] O. Fischer, *ibid.*, **7**, 1190 (1874).

[18] Elbs, *J. prakt. Chem.*, [2] **47**, 68 (1893).

[19] Cristol, Hayes and Haller, unpublished work.

[20] Bartlett, Mueller and Schneider, unpublished work.