117°,[14] 170–170.5°,[19] 167.5–169°,[15] 163°,[16] 164–165°,[17] sinter 163°, m.p. 171.5°.[18]

Anal. Calcd. for $C_{12}H_{12}N_4O_4$: C, 52.17; H, 4.38; N, 20.28. Found: C, 51.92; H, 4.35; N, 20.47.

Ethyl Δ²-Cyclohexenone-3-acetate (V).—A mixture of 11.7 g. (0.075 mole) of the monoketal (I), 13.4 g. (0.08 mole) of ethyl bromoacetate, 2 g. of cleaned granulated zinc, and a crystal of iodine was refluxed and stirred for 5.5 hours in 100 ml. of benzene. During this time fresh portions of zinc and iodine were added at half-hour intervals and after two hours another 13.4-g. portion of bromoester was added. Acidification of the reaction product with cold 10% sulfuric acid and extraction of the benzene solution with bicarbonate gave 2 g. of 1,3-cyclohexanedione. Fractionation of the neutral residue after removal of the benzene gave 5.0 g. (36%) of V; b.p. 108° (1 mm.); $n^{23}D$ 1.4879; λ_{max} 233 mμ (log ϵ 4.14).

Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 65.70; H, 7.55.

The dinitrophenylhydrazone melts at 107–108° after crystallization from alcohol.

Anal. Calcd. for $C_{16}H_{18}O_6N_4$: C, 53.03; H, 5.01; N, 15.46. Found: C, 53.04; H, 4.94; N, 15.83.

3-Cyano-Δ²-cyclohexenone (IV).—A solution of 24.7 g. (0.13 mole) of sodium metabisulfite in 40 ml. of water was added dropwise with stirring and cooling to 40 g. (0.256 mole) of the monoketal (I). To the resulting homogeneous solution was added 12.7 g. (0.26 mole) of sodium cyanide in 25 ml. of water. The mixture was stirred at room temperature for 20 hours; it was then filtered, and the filtrate was extracted with ether. The ether was removed and to the residue was added 40 ml. of 3 *N* hydrochloric acid; the homogeneous solution was allowed to stand 24 hours during which time the product separated from solution. The aqueous solution was saturated with ammonium sulfate, extracted with ether, the ether was removed, and the residue was fractionated to give 16.8 g. (54%) of the cyanoketone (IV); b.p. 105° (3.8 mm.); $n^{21}D$ 1.5104; λ_{max} 236 mμ (log ϵ 4.08).

Anal. Calcd. for C_7H_7NO: C, 69.40; H, 5.82; N, 11.57. Found: C, 69.11; H, 5.94; N, 11.97.

Both the crude cyanohydrin and the unsaturated cyanoketone gave the same dinitrophenylhydrazone; m.p. 204–204.5° after recrystallization from ethanol.

Anal. Calcd. for $C_{13}H_{11}N_5O_4$: C, 51.83; H, 3.68; N, 23.25. Found: C, 51.68; H, 3.89; N, 22.88.

The cyanoketone readily formed an ethylene ketal; b.p. 96° (1 mm.); $n^{19}D$ 1.4968.

Anal. Calcd. for $C_9H_{11}O_2N$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.03; H, 6.92; N, 8.14.

3-Ethoxy-Δ²-cyclohexenone (VI).—A mixture of 1,3-cyclohexanedione (28 g., 0.25 mole), 50 ml. of absolute ethanol and a few crystals of *p*-toluenesulfonic acid in 500 ml. of benzene was allowed to reflux under a modified Dean–Stark trap for 16 hours. Removal of the solvent and fractionation of the residue gave 24.8 g. (71%) of the enol ether (VI)[20]; b.p. 76° (1.0 mm.); $n^{23}D$ 1.5030. The enol ether gave no derivative with the D.N.P. solution.

Diethyl 3-Carboxymethylene-Δ²-cyclohexenylacetate (**VII**).—Application of the Reformatsky reaction to 10 g. of the enol ether, using the same conditions as for the monoketal, gave 6.8 g. (37%) of a product, b.p. 110° (1 mm.), $n^{17}D$ 1.5311, λ_{max} 298 mμ (log ϵ 4.44).

Anal. Calcd. for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 66.56; H, 8.16.

When the reaction was carried out with less bromoester a mixture of mono- and disubstituted products was obtained. From 9.5 g. of enol ether (VI) and 15 g. of ethyl bromoacetate there was obtained 6.8 g. of a product with a b.p. of 108–109° (1.0 mm.); $n^{24}D$ 1.5178; λ_{max} 233 mμ (log ϵ 3.86) and 298 mμ (log ϵ 4.32).

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(14) F. C. Whitmore and G. W. Pedlow, *ibid.*, **63**, 758 (1941).

(15) K. Dimroth and K. Resin, *Ber.*, **75B**, 322 (1942).

(16) A. J. Birch, *J. Chem. Soc.*, 430 (1944).

(17) A. J. Birch, *ibid.*, 1270 (1947).

(18) M. Orchin, This Journal, **66**, 535 (1944).

(19) H. Adkins and G. Rossow, *ibid.*, **71**, 3836 (1949).

(20) Woods and Tucker[6] prepared the enol ether by the action of ethyl iodide on the silver salt of 1,3-cyclohexanedione. The azeotropic method with *p*-toluenesulfonic acid as a catalyst has been used recently on substituted 1,3-cyclohexanediones by R. L. Frank and H. K. Hall, *ibid.*, **72**, 1645 (1950).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Mechanisms of Elimination Reactions. VI. The Kinetics of Dehydrochlorination of Various 2,2-Diarylchloroethanes[1,2]

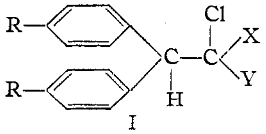
BY STANLEY J. CRISTOL, NORMAN L. HAUSE, ALFRED J. QUANT, HAROLD W. MILLER, KENDRICK R. EILAR AND JOHN S. MEEK

RECEIVED DECEMBER 21, 1951

A study of the kinetics of dehydrochlorination of fourteen para substituted 2,2-diaryl-monochloro-, -dichloro- and -trichloroethanes with ethanolic sodium hydroxide at various temperatures has been conducted, and the energies and entropies of activation have been calculated. A discussion of the effects of increasing alpha chlorine substitution upon dehydrochlorination reactivities and upon the energies of activation is included.

No systematic study of the effects of adding halogen atoms to the α-carbon atom of alkyl halides in their second-order elimination of the elements of hydrogen halide with alkali seems to have been made. In the course of our work on elimination reactions, it seemed worthwhile to initiate such a study.

The compounds studied were of the type



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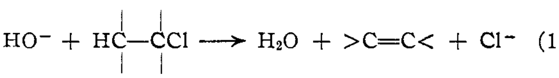
where X and Y may be hydrogen or chlorine atoms, and the reactions studied were of the type



$$HO^- + HC{-}CCl \longrightarrow H_2O + {>}C{=}C{<} + Cl^- \quad (1)$$

Some of the data desired have already been published,[3] but this paper completes the work on these

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[1] This work was supported by the Office of Naval Research and was presented in part before the Division of Organic Chemistry at the San Francisco Meeting of the American Chemical Society, March, 1949.

[2] Previous paper in series: S. J. Cristol and N. L. Hause, This Journal, **74**, 2193 (1952).

[3] S. J. Cristol, *ibid.*, **67**, 1494 (1945).

compounds and reports work for a total of fourteen compounds. Reaction-rate constants were obtained for dehydrochlorination with sodium hydroxide in 92.6 weight per cent. ethanol at three temperatures for six trichloro compounds of type I (X = Y = Cl), hereinafter called "DDT" compounds, with R = CH_3, CH_3O, H, F, Cl or Br, six similarly constituted dichloro compounds (I, X = Cl, Y = H), hereinafter called "DDD" compounds and two monochloro compounds (I, X = Y = H), hereinafter called "DDM" compounds, with R = Cl or Br.

Solutions of known halide and hydroxide concentrations were prepared, and the rates were followed by titration for chloride ion of aliquots removed at various times during the course of a run. The method used was similar to that previously described.[3]

Satisfactory values were obtained with the second-order rate expression (first order in halide concentration and first order in hydroxide ion concentration) for all of the compounds studied. In each case almost exactly one mole of chloride ion was produced per mole of halide after long intervals of time. In the case not previously studied, it was shown that the corresponding olefin was produced by action of sodium hydroxide on the halide. Table I presents the data and results of these experiments.

The experimental energies of activation, E_{act}, were calculated from the data of Table I in the usual fashion. These values, combined with values of the reaction-rate constants k corresponding to a temperature of 30° (obtained from the plots of log k vs. $1/T$) were used in the appropriate equation[4] to calculate values for the entropies of activation $\Delta S^{\ddagger}$. The values for energies and entropies of activation are given in Table II. The estimated uncertainties in E_{act} are 0.3 kcal./mole and in $\Delta S^{\ddagger}$, about 0.8 cal. per degree per mole.

Table I

Data and Reaction-rate Constants for Dehydrochlorination with Sodium Hydroxide in 92.6% Ethanol of Type I Compounds

Para substituent R	Temp., °C.	Halide, M	NaOH, M	Rate constant, 10^5k liters/sec./mole		Average deviation, %
					Av	
(a) DDT Compounds (I, X = Y = Cl)						
CH_3O	20.11				9.18^{a}	0.0
	30.37				30.3^{a}	1.2
	40.19	0.01000	0.05353	97.8	97.2	0.7
		.01000	.05353	96.5		
CH_3	20.11				10.9^{a}	0.0
	30.37				36.9^{a}	.0
	40.19	.01003	.05353	110	111	.9
		.01001	.05353	112		
H	20.11				36.9^{a}	0.4
	30.37				127^{a}	1.0
	40.19	.01002	.05353	352		
		.01002	.05353	350	351	0.3
F	20.11				303^{a}	0.8
	30.37				940^{a}	1.7
	40.19	.00998	.05353	2630	2670	1.3
		.00999	.05353	2700		
Cl	20.11				2480^{a}	2.5
	30.37				7110^{a}	2.1
	40.19	.00201	.01071	18700	18600	0.5
		.00200	.01071	18500		
Br	20.11				3470^{a}	1.2
	30.37				10300^{a}	1.0
	35.24	.00199	.01071	17300	17000	1.8
		.00200	.01071	16700		
(b) DDD Compounds (I, X = H, Y = Cl)						
			NaOH b, M			
CH_3O	19.95	0.01000	0.05349	3.33	3.36	0.8
		.00986	.05349	3.38		
	29.96	.01002	.05361	12.6	12.6	.4
		.01005	.05361	12.5		
	40.19	.01001	.05353	42.8	42.7	.4
		.00998	.05353	42.5		
CH_3	19.95	.01003	.05349	4.33	4.33	.1
		.01004	.05349	4.32		
	29.96	.01000	.05361	15.7	15.7	.0
		.01001	.05361	15.7		
	40.19	.01000	.05353	51.8	51.0	1.6
		.01000	.05353	51.0		
		.00999	.05353	50.2		
H	19.95	.01000	.05349	14.3	14.3	0.0
		.01002	.05349	14.3		
	29.96	.01001	.05361	51.2		
		.01007	.05361	51.0	51.1	.2
	40.19	.01004	.05353	162		
		.01001	.05353	162	162	.0
F	19.95	.01005	.05349	70.7	71.0	.4
		.01003	.05374	71.3		
	29.96	.01005	.05361	232	235	1.1
		.01002	.05361	237		
	40.19	.00995	.05353	775		
		.01002	.05353	773	774	0.1
Cl	19.95	.01002	.05374	567	568	0.1
		.01001	.05374	568		
	29.96	.00999	.05361	1660	1660	.3
		.01000	.05361	1650		
	40.19	.00400	.02141	5250	5240	.2
		.00400	.02141	5230		
Br	19.95	.01002	.05349	777	776	.1
		.01001	.05349	775		
	29.96	.01011	.05361	2390	2380	.4
		.01009	.05361	2370		
	40.19	.00400	.02141	7630	7570	.8
		.00400	.02141	7510		
(c) DDM Compounds (I, X = Y = H)						
			NaOH a, M			
Cl	20.11				91.0^{a}	0.7
	30.37				282^{a}	2.1
	40.12	0.004970	0.05621	854	849	0.6
		.005049	.05621	844		
Br	20.06	.009951	.05621	126	126	.4
		.008667	.05621	127		
	29.69	.01001	.05621	405	406	.1
		.01009	.05621	406		
	40.12	.01022	.05621	1170	1170	.0
		.005249	.05597	1170		

[a] Data obtained from previous work.[3]

Discussion of Results

We wish first to discuss the effects of adding halogen atoms to the system with fixed para substituents. It will be noted from the data of Table I that the DDT (trichloro) compounds have specific reaction-rate constants (at 30°) 2.4 to 4.3 times as great as the DDD (dichloro) compounds, and the dichloro compounds, 5 to 6 times those of the DDM (monochloro) compounds, that is, the addition of halogen atoms to the α-carbon atoms of the alkyl halide results in an increased reactivity toward dehydrochlorination with ethanolic sodium hydroxide. It is to be noted particularly, however, that the increases in reactivity are due to different effects as indicated by the quantities of activation in Table II.

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(4) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 199.

TABLE II

ENERGIES AND ENTROPIES OF ACTIVATION FOR THE DEHYDROCHLORINATION OF TYPE I COMPOUNDS WITH SODIUM HYDROXIDE IN 92.6% ETHANOL

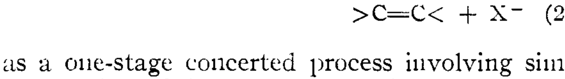
Para substituent	Compound type	E_{act} kcal./mole	ΔE_{act}[a] kcal./mole	$\Delta S^{\ddagger}_{300}$ cal./deg./mole	$\Delta\Delta S^{\ddagger}_{300}$[b] cal./deg./mole
CH_3O	DDT	21.4	1.6	−6.1	3.6
	DDD	23.0		−2.5	
CH_3	DDT	21.0	1.3	−7.1	2.7
	DDD	22.3		−4.4	
H	DDT	20.5	1.4	−6.5	2.9
	DDD	21.9		−3.4	
F	DDT	19.8	1.8	−4.6	3.3
	DDD	21.6		−1.3	
Cl	DDT	18.3		−5.5	
	DDD	20.1	1.8	−2.3	3.2
	DDM	20.2	0.1[c]	−5.8	−3.5[d]
Br	DDT	18.8		−3.0	
	DDD	20.6	1.8	0.0	3.0
	DDM	20.2	−0.4[c]	−5.0	−5.0[d]

[a] Difference in energy of activation of DDD and of DDT compound. [b] Difference in entropy of activation of DDD and of DDT compound. [c] Difference of energy of activation of DDM and of DDD compound. [d] Difference of entropy of activation of DDM and of DDD compound.

Thus, the increase in reactivity of the DDT compounds over the corresponding DDD compounds is a reflection of an *increase* in activation energy of approximately 1.6 kcal./mole for the dichloro compounds (equivalent to a factor of 14 in rate) compared with the trichloro compounds, this factor being partially compensated for by a corresponding *increase* in the molar entropy of activation of 3.1 entropy units (equivalent to a factor of approximately 5 in rate). On the other hand, the activation energies of the monochloro and dichloro compounds are substantially *identical*, and the decrease in reactivities of the DDM compounds compared with the DDD compounds is due entirely to a *decrease* in the entropy of activation.

We should like to consider the following tentative explanation of the activation energy data.

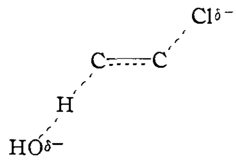
The removal of the elements of hydrogen halides from an alkyl halide by base in a second-order (E_2) elimination has generally been represented[2,5–9] to proceed as



(2)

as a one-stage concerted process involving simultaneous loss of the proton, formation of the carbon–carbon double bond and departure of halide ion.[10]

If the transition state for concerted E_2 elimination is represented as



then the energy of activation will be a function of (a) the ease of heterolytic fission of the carbon–hydrogen bond and (b) the ease of heterolytic fission of the carbon–chlorine bond assuming that the carbon–carbon bonds are similar in each case. (The validity of this assumption will be discussed below. It is likewise assumed that the solvation characteristics of the initial *vs.* the transition state are independent of the amount of chlorine substitution.) Unfortunately, direct measurements of either (a) or (b) are not available, but the argument from analogy proceeds as follows:

Taking the monochloro compounds as the basis for discussion, addition of more chlorine atoms to give the DDD and DDT compounds should lower the energy necessary to bring about the fission of the C–H bond into C^- and H^+, due to the negative inductive effect of chlorine (compare the acid strengths of mono-, di- and tri-chloroacetic acids).[11,12] This, then, should tend to decrease the energy of activation of the elimination process.[13]

Arguments regarding the effect of addition of chlorine atoms on the strength of the carbon–chlorine bond undergoing fission are not so straightforward, but here again certain analogies are available. Brockway[14] has measured the carbon–fluorine bond lengths in the fluoromethanes, and has observed a bond shortening in difluoromethane (1.36 Å.) as compared with methyl fluoride (1.42 Å.). This shortened bond length has been assumed to indicate a stronger carbon–fluorine bond. Addition of a third or fourth fluorine atom does not further shorten the bond. Although bond strengths (homolytic fission) and "ionic" bond strengths (heterolytic fission) are not necessarily parallel, it seems likely that there might be such a parallelism here and that one may conclude that addition of a second fluorine atom to fluoromethane stabilizes the carbon–fluorine bond markedly, whereas addition of the third and fourth atoms do not influence the bond strengths to as great a degree. Similar results are apparent from silicon–chlorine bond distances in the chlorosilanes[15–17] and the methylchlorosilanes[15,18,19] and have been discussed by Walsh.[20] Although any bond shortenings in the chloromethanes are too small to be significant experimentally,

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(5) E. D. Hughes and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 657 (1941).

(6) C. R. Hauser, THIS JOURNAL, **62**, 933 (1940).

(7) P. S. Skell and C. R. Hauser, *ibid.*, **67**, 1661 (1945).

(8) S. J. Cristol, *ibid.*, **69**, 338 (1947).

(9) M. L. Dhar, E. D. Hughes, C. K. Ingold, A. M. M. Mandour, G. A. Maw and L. I. Woolf, *J. Chem. Soc.*, 2093 (1948).

(10) This mechanism has been suggested as the usual one for "*trans*" elimination,[2,8] and thus presumably is involved for systems without restricted rotation around the carbon–carbon bond.

(11) G. N. Lewis, THIS JOURNAL, **38**, 762 (1916).

(12) H. B. Watson, "Modern Theories of Organic Chemistry," Second Edition, Oxford Press, 1941, p. 27.

(13) A. E. Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 219–222.

(14) L. O. Brockway, *J. Phys. Chem.*, **41**, 193 (1937).

(15) L. O. Brockway and F. T. Wall, THIS JOURNAL, **56**, 2373 (1934).

(16) L. O. Brockway and J. Y. Beach, *ibid.*, **60**, 1836 (1938).

(17) L. O. Brockway and I. E. Coop, *Trans. Faraday Soc.*, **34**, 1429 (1938).

(18) R. L. Livingston and L. O. Brockway, THIS JOURNAL, **66**, 94 (1944).

(19) R. L. Livingston and L. O. Brockway, *ibid.*, **68**, 720 (1946).

(20) A. D. Walsh, *Discussions Faraday Soc.*, **2**, 65 (1947).

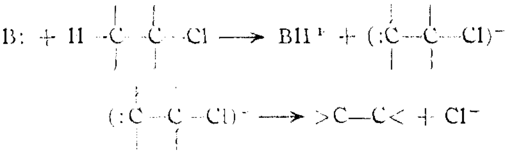
Walsh and Skinner and Sutton[21] give strong arguments for a strengthening of the carbon–chlorine bond in dichloromethane by the substitution of the second chlorine atom into methyl chloride, whereas the addition of a third atom does not bring about a corresponding increase in bond strength. This lessening of effect may well be due to the strong repulsive interactions between the non-bonded chlorine atoms, which are suggested to be responsible for the dipole moments observed for the chloromethanes.[22] These repulsions (similar to B-strain[23]) caused by overloading of the carbon atom by bulky negative groups, may operate to make the $-CCl_3$ system less stable than the $-CHCl_2$ system.

As the addition of each chlorine atom causes a decrease in the carbon–hydrogen bond strength, it is thus possible to explain the identical values for E_{act} for the DDM's and DDD's, addition of the second chlorine atom causing two opposite and equal effects. The lower value for E_{act} for the DDT's as compared with the DDD's may then be explained by the assumption that addition of the third chlorine atom decreases the carbon–hydrogen bond strength without a corresponding increase, and probably with a decrease, in the carbon–chlorine bond strength (see below).

A test of this tentative explanation is available in the work of van Romburgh[24] and of Prins.[25] The above discussion would suggest that treatment with alkali of a compound $CH_2ClCHRCHCl_2$ would result in elimination of the chlorine from the carbon bearing only one chlorine atom rather than from that bearing two, as the direction of the elimination would be a consequence only of the carbon–chlorine ionic bond strength, the hydrogen atom eliminated being common to both chlorine atoms. On the other hand, elimination from $CHCl_2CHRCCl_3$ might involve the trichloro system rather than the dichloromethyl system. These are indeed the experimental observations. Treatment of 1,1,3-trichloropropane with ethanolic potassium hydroxide gives principally 3,3-dichloropropene-1,[24] whereas 1,1,1,2,3,3-hexachloropropane gives 1,1,2,3,3-pentachloropropene-1.[25] These appear to be the only pertinent cases described in the literature.

In the above argument it was assumed that the chlorine atoms have no effect on the stabilities of the carbon–carbon single or double bonds. However, additional resonance stabilization of a vinyl halide system[5] in the product olefin would superimpose a decrease in activation energy with increasing chlorine substitution. This effect is not great enough to destabilize a dichloro system over a monochloro system; however, as indicated by our results and those of van Romburgh and Prins, although it may be responsible in part for the enhanced reactivity of the trichloro system.

It should be noted that it does not seem possible to explain the data satisfactorily in terms of an alternative carbanion mechanism[26] for second-order elimination, *viz.*



$$\mathrm{B{:}} + \mathrm{H}-\underset{|}{\overset{|}{\mathrm{C}}}-\underset{|}{\overset{|}{\mathrm{C}}}-\mathrm{Cl} \longrightarrow \mathrm{BH}^{+} + (:\underset{|}{\overset{|}{\mathrm{C}}}-\underset{|}{\overset{|}{\mathrm{C}}}-\mathrm{Cl})^{-} \quad (3a)$$

$$(:\underset{|}{\overset{|}{\mathrm{C}}}-\underset{|}{\overset{|}{\mathrm{C}}}-\mathrm{Cl})^{-} \longrightarrow {>}\mathrm{C}-\mathrm{C}{<} + \mathrm{Cl}^{-} \quad (3b)$$

If step (3a) is rate-determining, then the effect of adding chlorine atoms would very likely be cumulative. A mechanism involving step (3a) as reversible and (3b) as slow might conceivably be satisfactory, but until recently no evidence has been obtained to support such a mechanism in a dehydrohalogenation process.[7,26a]

As noted above, in addition to the regular differences in activation energies between series, there are also regular differences in entropy of activation, the dichloro series having approximately 4.2 e.u./mole more favorable activation entropy than the monochloro series, and the trichloro compounds being approximately 3.1 units less favorable than the dichloro compounds. These alternating terms, superimposed upon the values for the activation energies, make the reactivities of the series increase regularly from monochloro to dichloro to trichloro, at least at the temperatures studied.

A comparison of the values for E_{act} and $\Delta S^{\ddagger}$ within the DDM, DDD or DDT series is of interest. Hammett[27] 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 through a series of substituent constants σ, dependent only upon the nature and position of the substituent, and a series of reaction constants ρ which depend only upon the reaction series. These are interrelated by the equation

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

where k is the velocity or equilibrium constant of the reaction for the substituted organic reactant, and k_0 that for the unsubstituted reactant. We have previously reported[3] that a fairly satisfactory ρ–σ correlation may be made for the rate constants at 20.11° for the DDT's, a probable error in log k of 0.110 being observed, with values of ρ of 2.729 and of log k_0 of -2.822 being found. A similar treatment of the 19.95° data for the DDD's is given in Fig. 1, and corresponding values were $\rho = 2.456$, $\log k_0 = -3.430$ and probable error $r = 0.169$. The values for probable error r, which should be halved to compare with monophenyl compounds, are comparable in magnitude with those discussed by Hammett.

In Hammett's treatment of the ρ–σ correlation, it is assumed that the correlation is effective because the $\Delta S^{\ddagger}$ terms are constant within a reaction series. Thus the rate differences are supposed to be meas-

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(21) H. A. Skinner and L. E. Sutton, *Trans. Faraday Soc.*, **40**, 164 (1944).

(22) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1946, p. 135.

(23) H. C. Brown and R. S. Fletcher, THIS JOURNAL, **71**, 1845 (1949); **72**, 1223 (1950).

(24) M. P. van Romburgh, *Bull. soc. chim.*, **37**, 98 (1882).

(25) H. J. Prins, *J. prakt. Chem.*, **89**, 414 (1914).

(26) E. F. Landau, W. F. Whitmore and P. Doty, THIS JOURNAL, **68**, 816 (1946).

(26a) NOTE ADDED IN PROOF.—Recent deuterium exchange experiment run by L. C. Leitch and H. J. Bernstein, *Can. J. Research*, **28B**, 35 (1950), and by S. J. Cristol and D. D. Fix, unpublished work, suggest that the latter mechanism may be a strong possibility in certain cases.

(27) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter VII.

ures of differences in activation energies. This is often the case, but there are a number of exceptions.[28-31] Inspection of our data indicates that we have found another exception. The values of $\Delta S^{\ddagger}$ vary from −4.4 to 0.0 e.u. in the DDD series and from −7.1 to −3.0 e.u. in the DDT series, with a general, although not exact, trend to associate high values of $\Delta S^{\ddagger}$ with low values of E_{act}. This inverse relationship of E_{act} and $\Delta S^{\ddagger}$ is opposite to the direct relationship found previously in those cases where $\Delta S^{\ddagger}$ varies.

Materials Used

The trichloroethanes were the same as previously described.[3]

The following dichloroethanes were prepared by condensation of the appropriate aromatic compound with dichloroacetal: **1,1-dichloro-2,2-bis-(*p*-tolyl)-ethane**,[32] m.p. 78.5–79°; **1,1-dichloro-2,2-bis-(*p*-anisyl)-ethane**,[33] m.p. 114.5–115°; **1,1-dichloro-2,2-bis-(*p*-fluorophenyl)-ethane**,[34] m.p. 77.5–78.5°; **1,1-dichloro-2,2-diphenylethane**,[32] m.p. 77.5–78°; **1,1-dichloro-2,2-bis-(*p*-chlorophenyl)-ethane**,[35] m.p. 108–109°; **1,1-dichloro-2,2-bis-(*p*-bromophenyl)-ethane**, m.p. 134–135°.[36]

2-Chloro-1,1-bis-(*p*-bromophenyl)-ethane.—*p*-Bromophenacyl chloride was prepared in 88% yield by the Friedel–Crafts method as described by Collet.[37] It was also prepared in 88% yield by chlorination of *p*-bromoacetophenone following the procedure of Scholl and Korten[38] for the chlorination of acetophenone. After recrystallization from 95% ethanol or Skellysolve B (petroleum ether, b.p. 60–70°), it melted at 116–117°. The phenacyl chloride was reduced to *p*-bromostyrene chlorohydrin following the general procedure for the Meerwein–Pondorff–Verley reduction.[39] A mixture of 54 g. (0.23 mole) of *p*-bromophenacyl chloride, 47 g. (0.23 mole) of aluminum isopropoxide and 200 ml. of anhydrous isopropyl alcohol was heated for 18 hours, with acetone being removed by distillation through a 15-inch helices-filled Hempel column during the course of the reaction. The reaction mixture was worked up in the usual fashion, and the product was distilled under reduced pressure from finely powdered calcium carbonate. The product, **p-bromostyrene chlorohydrin**, boiled at 145–150° (4 mm.), had $n^{20}{}_{\text{D}}$ 1.5844, and was obtained in 92% yield (50 g.). The compound had a licorice odor and a sweet, stinging taste. It was not stable and darkened rapidly. Satisfactory analytical data could not be obtained.

To a mixture of 40.1 g. (0.17 mole) of *p*-bromostyrene chlorohydrin and 45 g. (0.27 mole) of bromobenzene in a flask equipped with a mechanical stirrer, 160 ml. of 100% sulfuric acid was added dropwise over a period of one hour. The temperature was maintained at 10° by external cooling. The reaction mixture began to solidify when about one-fourth of the acid was added. Stirring at 10° was continued for 3 additional hours, after which the mixture was poured onto ice. The solid was removed by filtration, and one recrystallization from methanol gave 44.5 g. (71%) of crude 2-chloro-1,1-bis-(*p*-bromophenyl)-ethane, m.p. 94–98°. Treatment of a Skellysolve B solution with an activated alumina column, followed by recrystallization from Skellysolve B or methanol gave white crystals, m.p. 97–97.5°.

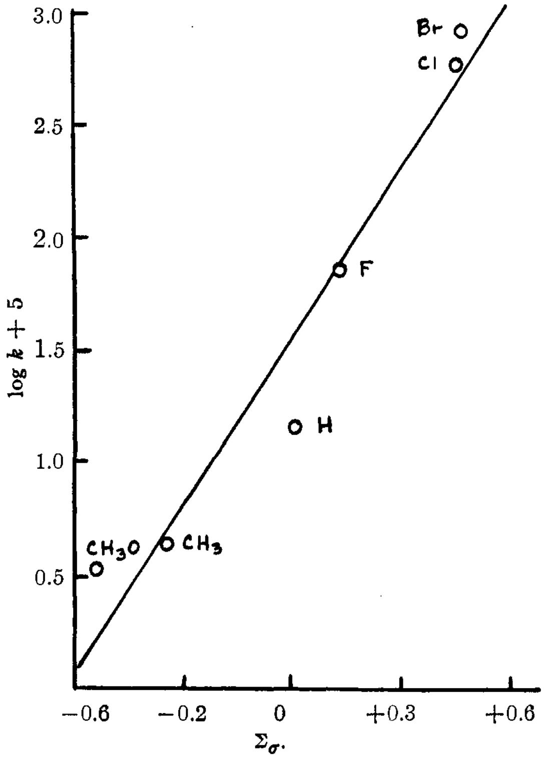

Fig. 1.—Relationship between log *k* of dehydrochlorination reaction and substituent constant.

Anal. Calcd. for $C_{14}H_{11}ClBr_2$: C, 44.89; H, 2.95. Found: C, 44.97; H, 3.07.

The structure of this compound was proved by dehydrochlorination with ethanolic sodium hydroxide to the known[40] **1,1-bis-(*p*-bromophenyl)-ethene**, m.p. 87–88.5°, and by oxidation of this olefin with chromic anhydride in glacial acetic acid to the known[41] *p,p'*-dibromobenzophenone, m.p. 174–175°.

2-Chloro-1,1-bis-(3-nitro-4-bromophenyl)-ethane was prepared by heating 500 mg. of 2-chloro-1,1-bis-(*p*-bromophenyl)-ethane with 5 ml. of fuming nitric acid at 50° for 30 minutes. The product, after recrystallization from 95% ethanol, melted at 111–112.5°.

Anal. Calcd. for $C_{14}H_9Br_2ClN_2O_4$: N, 6.03. Found: N, 5.88.

2-Chloro-1,1-bis-(3,5-dinitro-4-bromophenyl)-ethane was prepared by heating 500 mg. of 2-chloro-1,1-bis-(*p*-bromophenyl)-ethane with a mixture of 5 ml. of fuming nitric acid and 5 ml. of concentrated sulfuric acid on the steam-bath for one hour. After recrystallization from acetone–ethanol, it melted at 223–223.5°.

Anal. Calcd. for $C_{14}H_7Br_2ClN_4O_8$: N, 10.10. Found: N, 10.23.

2-Chloro-1,1-bis-(*p*-chlorophenyl)-ethane was prepared in a similar fashion to the *p*-bromo analog.[42,43] It melted at 51–51.5°.

All of the olefins, with one exception, produced by the dehydrochlorination reaction described in this work are described in the literature. The exception, **2-chloro-1,1-bis-(*p*-fluorophenyl)-ethene**, was prepared by dehydrochlorination of the corresponding saturated compound with ethanolic sodium hydroxide and melted at 34.5°.

Anal. Calcd. for $C_{14}H_9ClF_2$: C, 67.1; H, 3.6. Found: C, 67.0; H, 3.7.

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[28] E. W. Timm and C. N. Hinshelwood, *J. Chem. Soc.*, 862 (1938).

[29] G. E. K. Branch and A. C. Nixon, THIS JOURNAL, **58**, 2499 (1936).

[30] G. N. Burkhardt, C. Horrex and D. I. Jenkins, *J. Chem. Soc.*, 1649 (1936).

[31] W. C. Davies, *ibid.*, 1865 (1938).

[32] W. P. Buttenberg, *Ann.*, **279**, 325 (1894).

[33] H. Wiechell, *ibid.*, **279**, 338 (1894).

[34] P. Müller, *Helv. Chim. Acta*, **29**, 1560 (1946).

[35] H. L. Haller, P. D. Bartlett, N. L. Drake, M. S. Newman and co-workers, THIS JOURNAL, **67**, 1591 (1945).

[36] K. Brand and D. Krücke-Amelung, *Ber.*, **72**, 1029 (1939).

[37] A. Collet, *Compt. rend.*, **125**, 717 (1897).

[38] R. Scholl and H. Korten, *Ber.*, **34**, 1902 (1901).

[39] A. L. Wilds in R. Adams, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1944, Vol. II, p. 200.

[40] J. N. Ashley, J. F. Grove and T. Henshall, *J. Chem. Soc.*, 261 (1948), report an m.p. of 84° for this compound.

[41] F. Bodroux, *Compt. rend.*, **137**, 710 (1903), reports an m.p. of 171–172° for this compound.

[42] P. D. Bartlett, G. P. Mueller and A. Schneider, unpublished work.

[43] We are indebted to Mr. L. H. Cummings for this preparation.