with $H_2C_2O_4$ will have a higher temperature coefficient than the reaction of Co^{+++} with Fe^{++}. The results of experiments 10 and 11 show that inhibition by Co^{++} can indeed be realized by proper choice of conditions.

Two further points of comparison between the work on the reaction of chlorine and maleic acid, and the present work seem worthy of mention. The observation that all of the ions discussed here acted as inhibitors for the former reaction whereas some act as positive catalysts in the present study correlates with the slower reaction of the higher valence states (demonstrated for Ce^{++++}) with maleic acid as compared to oxalic acid. Inhibition by oxygen was marked in the former reaction; no significant effect of oxygen over a wide range of conditions was observed in the reaction under present study however.

Acknowledgment.—The author wishes to thank Dr. T. R. Rubin for helpful discussion of this work, and Miss Ilse L. Hochhauser for help with some of the experiments.

Summary

Results on the rate and kinetics of the reaction of chlorine with oxalic acid induced by ferrous ion, over a wide range of conditions are presented.

The data are interpreted by a chain mechanism involving atomic chlorine; this substance results from the reaction of ferrous ion with chlorine.

As the ratio of chlorine to oxalic acid decreases, the chain breaking step changes from an association of atomic chlorine to a reaction of this substance with the oxalate free radical.

Atomic chlorine reacts more rapidly with $HC_2O_4^-$ than with $H_2C_2O_4$. The activation energy of the former reaction is about 7,000 cal. and its pz factor about 5×10^{12}.

NH_4^+, VO^{++}, Ce^{+++}, Mn^{++}, Co^{++}, Cu^{++}, Ni^{++} and Pr^{+++} affect the rate of the reaction. Under the most usual conditions NH_4^+, VO^{++}, Ce^{+++} and Mn^{++} act as inhibitors, while the remaining ions enhance the induced effect.

Only VO^{++} functions as a simple inhibitor. The kinetics observed prove that atomic chlorine reacts with VO^{++}; the activation energy of this reaction is about 5,000 cal.

For the other metal ions, reaction of the upper valence state of the inhibitors with oxalic acid must also be considered. With Ce^{+++} and Mn^{++}, the effect of the reaction of the upper valence states with Fe^{++} or the oxalate free radical predominates in most of the experiments over the effect produced by reaction with oxalic acid; with Cu^{++}, Ni^{++}, Pr^{+++} and Co^{++}, the reverse is true.

The mechanism predicts conditions under which a negative catalyst can enhance the rate of reaction (observed for Ce^{+++}) and a positive catalyst can become an inhibitor (observed for Co^{++}).

ITHACA, N. Y. RECEIVED DECEMBER 17, 1945

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Dipole Moments of Chlorobenzene, Monochlorocyclopropane, and 1,2-Dichlorocyclopropane, with a Calculation of the Exterior Valence Angle of the Cyclopropane Ring[1]

BY BERNARD I. SPINRAD

In recent years, dipole moments have been determined for the most part from radio frequency capacity data. While there is no objection to such procedures so long as dispersion is negligible, it appears that audio frequency bridge methods have been neglected for this purpose, although they form the basis for much of the work of testing engineers.[2] This is despite the fact that the only serious objection to them is that conductance effects, which are hardly ever appreciable in dilute solutions of low dielectric constant, may in rare cases be troublesome. The method, moreover, has several advantages: easy construction of the apparatus, complete elimination of dispersion and stray inductive effects, and simplicity of computation combined with ability to evaluate the effect of small conductance leakages.

During the course of work on physical chemical applications of the Schering Bridge, it was found that the apparatus was a highly accurate audio frequency capacity bridge. The molar polarizations and dipole moments of chlorobenzene, monochlorocyclopropane, and 1,2-*dl*-dichlorocyclopropane were thereupon measured with a view to investigating the convenience of the method. The measured moment of chlorobenzene is a check on the accuracy of the experiment, and the moments of the cyclopropanes are useful in determining whether the dichlorocyclopropane is *dl* or *meso*, and, further, in approximating the angle which the carbon–chlorine bond makes with the plane of the carbon ring.

Experimental

Materials.—1,2-*dl*-Dichlorocyclopropane and monochlorocyclopropane were prepared and purified by Dr. P. G. Stevens of this Laboratory.[3]

Chlorobenzene ("Paragon Labs., Tech.") was purified

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[1] This paper contains material from the dissertation presented by Bernard I. Spinrad to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] See, for example, B. Hague, "A. C. Bridge Methods," Pitman, London, 1938.

[3] See the accompanying paper by Dr. P. G. Stevens.

by double fractionation through a Widmer column (n^{25}_{D} 1.5220).

Benzene ("Baker's Thiophene-free") was crystallized five times by freezing and fractionally distilled over activated alumina in a four foot column packed with cylindrical helices. The middle 60% was collected over activated alumina in glass stoppered flasks, and handled with a syringe.

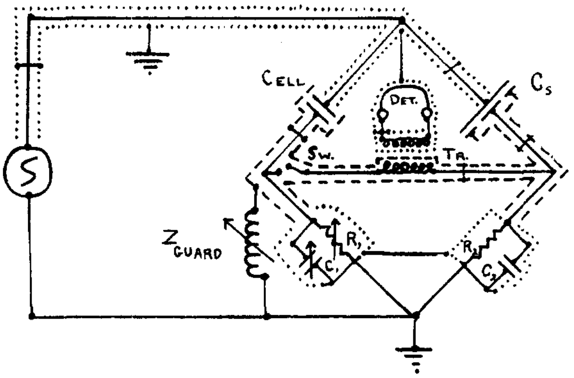

Fig. 1.—. . . . ., Ground shielding; — — — — — —, guard shielding.

Bridge.—The bridge circuit is diagramed in Fig. 1. C_s is a standard air condenser made of concentric brass tubing, containing a guard ring, and so arranged as to have no solid dielectric in the field; it is thus, for our purposes, loss free. Its value, as determined by calibration in the bridge against standard mica condensers, is 50.37 $\mu\mu$F. The cell is the smaller one of those previously used by Akerlof and Short,[4] around which lead foil has been formed to act as a guard ring. The low voltage arms contain calibrated five dial decade resistors in parallel with small variable air condensers. The detector used in this work was a cathode ray null detector, coupled to the bridge by means of a shielded transformer; an amplifier and phones was found, however, to be equally sensitive. All connections were shielded either to ground or to the guard circuit, and the guard circuit was balanced to the same phase and potential as the detector terminals by means of the guard impedance, consisting of resistors, capacitors, and inductors variously connected. The bridge was energized by a beat frequency oscillator and amplifier, capable of delivering several hundred volts at all audio frequencies. Generally, R_1 and C_1 were fixed, and balance obtained by adjusting R_2 and C_2. C_{cell} may then be calculated from

$$C_{\text{cell}} = \frac{R_2C_s}{R_1} \qquad (1)$$

or from

$$C_{\text{cell}} = \frac{R_2C_s}{R_1}\left(\frac{1 + \omega^2R_1C_1R_2C_2}{1 + \omega^2R_2{}^2C_2{}^2}\right) \qquad (2)$$

if there is appreciable conductance leakage.

Dilution.—Solutions were made up by weight into glass-stoppered flasks, and dilutions made by volume, a 100-ml. volumetric flask being calibrated for delivery volume of two fillings of a 50-ml. pipet. Fifty ml. of concentrated solution was pipetted in and benzene added to the mark, care being taken to keep all liquids at 25°. Since the cell holds about 70 ml. of solution, a part of its contents had to be used for the next dilution, and consequently, the data of any given run could not be checked. About 15 ml. of solution was used for rinsing the cell, and discarded.

Refractivities.—In the case of chlorobenzene, the refractivity was determined directly, using an Abbe refractometer and standard density values.[5] The refractivity of the dichlorocyclopropane was measured by Dr. Stevens,[3] while atomic refractivity data[6] were used for monochlorocyclopropane. All refractivity data are referred to the sodium D line.

Densities.—Densities were measured in one of the pycnometers described by Wood and Brusie, and the calibration of Brusie was used.[7]

Cell and Method of Measurement.—The cell was cleaned and baked before each dipole run, and it was found that this operation slightly affected the cell constants. Other types of manipulation had no effect on capacity, and the dimensions were therefore assumed to be constant during a run.

In order to take into account the effects of residual capacities through the glass envelope, the capacities of the empty cell and of the cell filled with stock benzene were measured during the course of each run. The dielectric constant of benzene at 25° was taken as 2.2770, the mean of several values given in recent literature,[8] and the residual capacity, x, calculated from

$$2.2770 = \frac{C_{\text{BENZENE}} - X}{C_{\text{EMPTY}} - X} \qquad (3)$$

The dielectric constant of any solution, referred to benzene at 25° as 2.2770, may then be calculated from

$$\epsilon = \frac{C - X}{C_{\text{EMPTY}} - X} \qquad (4)$$

Temperature.—The cell was thermostated at 25° in an oil-bath whose maximum temperature variation was 0.02°.

Calculation of Molar Polarization

The molar polarization was calculated by the method of Hedestrand,[9] using the formula

$$P_\infty = \lim_{c \to 0} \left\{ \frac{3000}{(\epsilon_0 + 2)^2} \frac{\delta\epsilon}{c} + \left(\frac{\epsilon_0 - 1}{\epsilon_0 + 2}\right)\left(\frac{1}{\alpha_0}\right)\left(M_2 - 1000\,\frac{\delta\alpha}{c}\right) \right\} \qquad (5)$$

The values of $\delta\epsilon/c$ and $\delta d/c$ were obtained by least squaring the data to a linear formula, since no deviation from linearity could be observed on a plot.

Recent data on the molar polarization of chlorobenzene in benzene solution have been calculated in various ways, with comparatively large discrepancies.[10] A check on the computations shows that the data are consistent, and that the discrepancies depend for the most part on the method of calculation, with Hedestrand's and similar methods giving higher values, while extrapolation of apparent polarization leads to lower values.

Neither method can actually claim to report experimental results at extreme dilution, since

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(4) G. Akerlof and O. A. Short, THIS JOURNAL, **58**, 1241 (1936).

(5) "International Critical Tables," Vol. III, 1st ed., McGraw Hill Book Co., Inc., New York, N. Y., p. 29.

(6) Getman and Daniels, "Outlines of Theoretical Chemistry," John Wiley and Sons, New York, N. Y., 1941, p. 86.

(7) S. E. Wood and J. P. Brusie, THIS JOURNAL, **65**, 1891 (1943); J. P. Brusie, Dissertation, Yale University, 1943.

(8) Anzilotti and Curran, THIS JOURNAL, **65**, 607 (1943); Turkevich, Oesper and Smyth, *ibid.*, **64**, 1170 (1942); Oesper, Lewis and Smyth, *ibid.*, **64**, 1130 (1942); Oesper and Smyth, *ibid.*, **64**, 173, 768 (1942); Oesper, Smyth and Kharasch, *ibid.*, **64**, 937 (1942).

(9) G. Hedestrand, *Z. physik. Chem.*, (B) **2**, 428 (1929).

(10) Davis, Bridge and Svirbely, THIS JOURNAL, **65**, 859 (1943); Maryott, *ibid.*, **63**, 3079 (1941); Müller, *Physik. Z.*, **38**, 283 (1937).

the data always scatter with decreasing concentration. The use of least squaring the dielectric constant and density data to apply to Hedestrand's formula has, however, two advantages: first, errors in solvent dielectric constant are less critical; second, the dielectric constant data generally fit a smoother curve than do the apparent polarization data.

Experimental Results

Tables I and II summarize the experimental data. Table I lists dielectric constants, ϵ, densities, d, and molarities, c, as well as the calculated residual capacities, x, and the capacity of the empty cell. Below each set of measurements is given a pair of least squared linear formulas to describe the data.

TABLE I

DIELECTRIC CONSTANT AND DENSITY DATA

c	d	e	
	Chlorobenzene		
0.19336	0.87824	2.3392	$x = 0.256\mu\mu$ F
.09824	.87608	2.3078	$C_{\text{empty}} = 12.096\mu\mu$ F
.04912	.87491	2.2919	
.02456	.87434	2.2848	
0	.87380	2.2770	
	$d = 0.87381 + 0.02396c$		
	$e = 2.2766 + 0.3211c$		
	Monochlorocyclopropane		
c	d	e	
0.24727	.87601	2.3664	$x = 0.318\mu\mu$ F
.12363	.87487	2.3229	$C_{\text{empty}} = 12.036\mu\mu$ F
.06181	.87431	2.2995	
.03091	.87404	2.2886	
0	.87376	2.2770	
	$d = 0.87375 + 0.00910c$		
	$e = 2.2774 + 0.3613c$		
	1,2-Dichlorocyclopropane		
c	d	e	
0.4728	0.88847	2.3495	$x = 0.336\mu\mu$ F
.2364	.88104	2.3124	$C_{\text{empty}} = 12.066\mu\mu$ F
.1182	.87739	2.2947	
.0591	.87560	2.2863	
0	.87377	2.2770	
	$d = 0.87374 + 0.03109c$		
	$e = 2.2769 + 0.1530c$		

TABLE II

CALCULATION OF DIPOLE MOMENTS

Substance	P	R	μ
Chlorobenzene	83.26	31.18	1.60
Monochlorocyclopropane	82.32	18.76	1.76
1,2-*dl*-Dichlorocyclopropane	52.38	23.87	1.18

Table II gives molar polarizations, P, molar refractivities, R, and dipole moments expressed in Debye units (μ). The latest physical constants were used in calculating dipole moments, the formula leading to

$$\mu = 0.01281\sqrt{(P - R)T} \qquad (6)$$

Discussion of Results

The calculated moment of chlorobenzene may serve as a check on the results obtained with this circuit. From the literature,[10,11] the value of 1.59 Debyes seems to be the most probable one for the moment of chlorobenzene in benzene solution when polarization is calculated by the method of this paper. The value obtained here is 1.60 Debyes, in close agreement.

Although the possibility of impurity of the samples is a limiting factor, the electric dipole moments of the chlorocyclopropanes may be used to estimate the exterior valence angle of the cyclopropane ring, if we assume that the moments measured here are consistent with the law of vector addition of bond moments. This involves the assumption that effects of mutual polarization of the carbon–chlorine bonds and induction are small.

If, now, the planes of the exterior valence bonds of the chlorocyclopropanes bisect the C–C–C angles, as is to be expected from symmetry, and if the carbon ring is taken as an equilateral triangle, the dipole moment of the *dl*-(*trans*)-1,2-dichlorocyclopropane may be calculated from

$$\mu = \mu_0 \cos \alpha \qquad (7)$$

μ_0 being the single carbon–chlorine bond moment (taken as the dipole moment of monochlorocyclopropane) and α, the angle which the carbon–chlorine bond makes with its projection on the ring plane. For the *meso* (*cis*) compound, the formula would be

$$\mu = \mu_0 \sqrt{\cos^2 \alpha + 4 \sin^2 \alpha} \qquad (8)$$

Since $\mu = 1.18$ and $\mu_0 = 1.76$, we can readily see that formula 8 cannot be fitted to the data, $\mu = \mu_0$ being the smallest possible value for the dichlorocyclopropane moment. Substitution into formula 7, however, gives $\alpha = 48°$, which, under the assumption that the direction of the carbon–chlorine bond in relation to the plane of the carbon ring is the same as that of the carbon–hydrogen bond which it replaces, corresponds to an exterior valence angle of 96° for cyclopropane. The C–C–Cl angle for this model is then 125°. The fact that in the paraffin series, the bond angles show very little distortion due to substitution of chlorine for hydrogen[12] is partial justification for this last assumption.

If the dichlorocyclopropane measured contained impurities of high dipole moment (as the meso compound or the 1,1 compound) 1.18 is a higher moment than pure *dl*-1,2-dichlorocyclopropane would give, and the angle would actually be greater than 96°. 7% of meso compound or about 12% of 1,1-compound would bring the corrected result to the region of 120°.

Other investigators have obtained varying

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(11) The data of the first paper of reference 10 have been recalculated by the method used here to give $\mu = 1.59$ *D*.

(12) Beach and Stevenson, THIS JOURNAL, **60**, 475 (1938).

values for the bond angle. Smith[13] has calculated from the molecular moment of inertia of cyclopropane (obtained from analysis of the fine structure of the infrared spectrum) an angle of 136°, corresponding to a tetrahedral C–C–H angle; Donahue, Humphrey and Schomaker,[14] from electron diffraction studies of the similar spiropentane structure, have suggested a 120° H–C–H angle (which makes the C–C–H angle 115.5°). In view of the conflicting results which have been thus variously derived, a more accurate direct determination of the external valence angle of cyclopropane would be of interest.

One consideration which supports the small value of the bond angle indicated here is that, according to Dennison,[15] in the vibration spectrum of methane, the mode of vibration corresponding to simultaneous mutual approach of two pairs of hydrogen atoms has a lower frequency than the mode corresponding to alternate approach of the pairs. This would seem to indicate that a strain on one pair of tetrahedral bonds tending to decrease the angle between them (as in cyclopropane) also decreases the equilibrium value of the other bond angle. (In double bonded compounds such as ethylene, this effect may be counteracted by shortening of the bond distances.)

The value of 1.76 Debyes for the dipole moment of monochlorocyclopropane, midway between the single bond moment of a paraffinic carbon–chlorine bond (2.04)[16] and of an olefinic carbon–chlorine bond (*ca.* 1.5) is in harmony with the apparent inertness of the chlorine attached to the cyclopropane ring, and it is possible that the substituent reactivities of isopropyl chloride, chlorocyclopropane, and vinyl chloride follow the same order as their dipole moments. In any case, the intermediate value of the chlorocyclopropane is noteworthy.

Acknowledgment.—The author wishes to express his thanks to Dr. Herbert S. Harned, under whose direction these researches were undertaken, to Dr. P. G. Stevens for suggesting the study of the cyclopropane derivatives, and to Dr. Lars Onsager for his advice in regard to the theoretical discussion of the problem.

Summary

1. The dipole moments of chlorobenzene, 1,2-*dl*-dichlorocyclopropane, and monochlorocyclopropane have been measured in benzene at audio frequencies by a bridge method.

2. The structure of the above-mentioned dichlorocyclopropane has been found to be *dl*, and the external valence angle of the cyclopropane ring has been calculated from the dipole moment data.

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[13] Smith, *Phys. Rev.*, (2) **59**, 924 (1941).

[14] Donahue, Humphrey and Shomaker, THIS JOURNAL, **67**, 332 (1945).

[15] Dennison, *Rev. Mod. Phys.*, **12**, 206 (1940).

[16] C. P. Smyth, "Dielectric Constant and Chemical Structure," Chem. Cat. Co., New York, N. Y., 1931; Appendix.

NEW HAVEN, CONN. RECEIVED SEPTEMBER 24, 1945

[CONTRIBUTION FROM THE STERLING CHEMICAL LABORATORY OF YALE UNIVERSITY]

Some New Cyclopropanes with a Note on the Exterior Valence Angles of Cyclopropane

BY PHILIP G. STEVENS[1]

The reaction of cyclopropane with chlorine is mainly that of substitution.[2] The initial product, monochlorocyclopropane, however, reacts so readily with more chlorine that, unless special procedures are adopted,[3] the cyclic products actually isolated consist almost entirely of dichlorides, the 1,1 and the 1,2 in the approximate ratio of 40:1. This great preponderance of 1,1 over 1,2-chlorination is a notable exception to the Meyer–Herzfelder rule,[4] and also to the results of both Tischenko[5] (using chlorine) and Kharasch and Brown[6] (using sulfuryl chloride) with *n*-butyl chloride, but is in harmony with the high temperature chlorination reported by Rust and Vaughan.[7] Both these two similar types of chlorination illustrate the increased activity of the hydrogen atom attached to a carbon atom holding a chlorine atom, which activity becomes effective when no steric hindrance is present as in the cyclopropane derivatives, or is reduced to a minimum at the elevated temperature employed by Rust and Vaughan.

The 1,2-dichloride does not seem to have been described previously, although Petrenko–Kritschenko[8] reported its reaction with alkali. It is stable to bromine and permanganate, to zinc dust in boiling acetic acid, and gives no color with tetranitromethane. Attempts to determine the configuration by chromatographical resolution using sucrose were unsuccessful. Spinrad[9] however has shown from the dipole moment that it must have the *dl*-configuration, and that the angle α of the carbon–chlorine bond with the ring

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[1] Present address: The General Aniline and Film Corporation, Development Division, 247 Park Avenue, New York.

[2] Gustavson, *J. prakt. Chem.*, [2] **42**, 496 (1890); **43**, 396 (1891).

[3] Roberts and Dirstine, THIS JOURNAL, **67**, 1281 (1945).

[4] Herzfelder, *Ber.*, **26**, 2932 (1893).

[5] Tischenko, *C. A.*, **31**, 5754 (1937).

[6] Kharasch and Brown, THIS JOURNAL, **61**, 2142 (1939).

[7] Rust and Vaughan, *J. Org. Chem.*, **6**, 478 (1941).

[8] Petrenko–Kritschenko, *Ber.*, **62**, 589 (1929).

[9] Spinrad, THIS JOURNAL, **68**, 617 (1946).