

may be explained by the displacement of hydroxo groups from the surface of the alumina due to the tendency of anions to bind coördinately to the aluminum in the structure. Anions vary greatly in their ability to form stable coördination compounds with aluminum, and their efficiencies in this respect^{2,3} are in the same order as the *pH* effects observed (I), with the exception of the case of phosphate (which changed its *pH* by only a few hundredths of a unit). The solution of the latter (which would contain the monohydrogen phosphate ion in appreciable concentration after adjustment of the *pH* of the solution to 7.00) resisted change in *pH* because of efficient buffer action.

If the increase in the *pH* of a salt solution is due to displacement of hydroxo groups from the alumina with concomitant anion sorption, the magnitude of the effect should increase with the concentration of anion and with the mass of alumina. This was observed (II and III).

Our interpretation of the experiments in which various samples of hydrous alumina were used (IV) is that the extent of surface hydroxo groups varies with the temperature of preparation of the alumina. This interpretation would lead to the conclusion that samples "60" and "95" possess more surface hydroxo groups than does sample "26"—a conclusion, it should be noted, that was reached previously² on the basis of different experimental approaches.

(3) Clay and Thomas, *THIS JOURNAL*, **60**, 2384 (1938).

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Alkaline Degradation of Benzene Hexachloride

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Several early investigators have reported¹ that the α -form of benzene hexachloride (1,2,3,4,5,6-hexachlorocyclohexane) yielded 1,2,4-trichlorobenzene when heated with alcoholic potassium hydroxide, and Meunier² has reported a similar finding for the β -isomer. On the other hand, van der Linden³ found that supposedly pure α -isomer yielded predominantly the 1,2,4-trichlorobenzene but also the 1,2,3- and 1,3,5-trichlorobenzenes. Recently, both Slade⁴ and Chamlin⁵ have stated that alkaline dehydrochlorination of benzene hexachloride yields a mixture of the isomers of trichlorobenzene.

In the present study, it has been shown that the pure α , β , γ , Δ and ϵ isomers of benzene hexachloride react with 1 *N* ethanolic potassium hy-

droxide at reflux temperature to yield only the 1,2,4-trichlorobenzene in significant amounts.

Experimental⁷

Materials.— α -Isomer, m. p. 153–154°; β -isomer, m. p. 298–300°; γ -isomer, m. p. 112.2–113.8°; Δ -isomer, m. p. 136–137°; ϵ -isomer, m. p. 216–217°. The reference 1,2,4-trichlorobenzene was Eastman Kodak Company material, m. p. 15–16°, and was used without further purification.

Dehydrochlorination.—Exactly 10.00 g. (2.00 g. of the ϵ -isomer) of each isomer was refluxed with a 50% excess of 1 *N* ethanolic potassium hydroxide for two hours. The resulting mixture was cooled and filtered, and the filter cake of potassium chloride was washed with cold ethanol, dried and weighed. A portion of each sample of potassium chloride was analyzed for the chloride ion in the usual manner. To the combined filtrate and washings from each reaction mixture was added water until no new clouding resulted. Long centrifugation resulted in the clean separation of the oily trichlorobenzene, which was washed thoroughly, dried over calcium chloride and then distilled.

Mononitro Derivatives.⁸—Approximately 1 g. of the trichloro compound was dissolved in 5 g. of fuming nitric acid (sp. gr. 1.49), then the resulting yellow solution was poured onto crushed ice. The waxy yellow solid so obtained was washed thoroughly, then recrystallized from ethanol to a constant melting point.

Dinitro Derivatives.⁸—Approximately 1 g. of the mononitrotrichlorobenzene was redissolved in 5 g. of fuming nitric acid (sp. gr. 1.49) and 5 g. of concentrated sulfuric acid (sp. gr. 1.84) was added slowly. After refluxing for one hour, the resulting yellow solution was cooled and poured into 100 ml. of water. The pale yellow solid which separated was washed thoroughly with water, then recrystallized from ethanol to a constant melting point.

Anilino Derivatives.⁸—Approximately 1 g. of the dinitrotrichlorobenzene was mixed with 5 g. of aniline and heated for one hour on the water-bath. After cooling, the resulting red mixture was extracted several times with 6 *N* hydrochloric acid. The orange crystals were then filtered, washed with water, and recrystallized from benzene (large quantity of anilino compound) or from ethanol (small quantity of anilino compound) to a constant melting point.

Discussion

That the dehydrohalogenation treatment was, for all practical purposes, quantitative for each isomer is demonstrated by the data in Table I.

TABLE I
EXTENT OF ALKALINE DEHYDROHALOGENATION OF ISOMERIC BENZENE HEXACHLORIDES

Isomer	KCl residue, g.		% Cl ⁻ in residue	% Dehydrohalogenation ^a
	Expt.	Theor.		
α	7.61	7.69	93.0	92.1
β	7.64	7.69	100.0	99.4
γ	7.72	7.69	98.9	99.4
Δ	7.66	7.69	94.5	94.2
ϵ	1.53	1.54	95.0	94.2

^a Washing losses traceable to the solubility of potassium chloride in iced ethanol were not considered.

Distillation of the trichlorobenzenes (obtained in 80–90% over-all yields) and their subsequent conversions into crystalline mononitro, dinitro and anilino derivatives yielded compounds possessing the melting points recorded in Table II. For purposes of comparison, a specimen of known 1,2,4-trichlorobenzene was included in the derivative series, while the corresponding comparison

(7) All melting points are corrected.

(8) Huntress and Carten, *THIS JOURNAL*, **62**, 511 (1940).

(1) Mitscherlich, *Ann. Physik*, **35**, 370 (1833); Lesimple, *Ann.*, **137**, 122 (1866); Matthews, *J. Chem. Soc.*, **59**, 170 (1891).

(2) Meunier, "Beilstein," Vol. V, p. 23.

(3) van der Linden, *Ber.*, **45**, 239 (1912).

(4) Slade, *Chem. Ind.*, **40**, 314 (1945).

(5) Chamlin, *J. Chem. Ed.*, **23**, 283 (1946).

(6) These isomers were obtained through the courtesy of Dr. E. C. Britton of the Dow Chemical Company.

data for the 1,2,3- and 1,3,5- isomers were taken from the literature.⁸

TABLE II

DERIVATIVES OF TRICHLOROBENZENES FROM DEHYDROHALOGENATION OF ISOMERIC BENZENE HEXACHLORIDES

Source	B. p., °C.	M. p., °C.	Derivative, m. p., °C.		
			Mono-nitro	Dinitro	Anilino
α -Isomer	212-215	11	48-54	99-101	182-183
β -Isomer	210-215	14	55-58	103-104.5	182-183
γ -Isomer	207-214	13	53-58	103-104	183-184
Δ -Isomer	212-215	16	55-58	102-104	183-184
ϵ -Isomer	55-58	102-103.5	183-184
1,2,4-Trichloro- benzene	212-215	15	55-57	102-104	184-185
1,2,3-Trichloro- benzene ^a	218-219	53	55-56	92-93	136-138
1,3,5-Trichloro- benzene ^a	208	63.5	67-68	128.5	179-180

^a Huntress and Carten, ref. 8.

It is apparent from these data that the dehydrohalogenation product of each of the five isomers of benzene hexachloride under the conditions specified herein is almost exclusively 1,2,4-trichlorobenzene. The three derivatives of 1,2,4-trichlorobenzene may be designated precisely as 2,4,5-trichloro-1-nitrobenzene, 2,4,5-trichloro-1,3-dinitrobenzene and 2,6-dianilino-5-chloro-1,3-dinitrobenzene. Since the α -isomer (m. p. 157°) has been reported¹ to yield also traces of 2,4-dichlorophenol, 2,4,6-trichlorophenol, pyrocatechol and "other products" upon heating with water to 200° in a closed tube, it is reasonable to assume that traces of these materials occurred in the present investigation, although they were not isolated (cf. the yields in Table I).

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Dieterici's Equation Modified

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One of the early attempts to improve on the van der Waals equation of state is the equation

$$p = \frac{RT}{v-b} e^{-a/vRT} \quad (1)$$

proposed by Dieterici¹ on semi-empirical grounds. The equation has been studied by several investigators^{2,3,4} and has been found to possess certain advantages over the van der Waals equation.

Dieterici's equation, however, has achieved its greatest success in a modified form

$$p = \frac{RT}{v-b} e^{-aT_c^{1/2}/vRT^{3/2}} \quad (2)$$

(1) C. Dieterici, *Wied. Ann.*, **69**, 685 (1899).

(2) J. H. Jeans, "The Dynamical Theory of Gases," Cambridge University Press, 1916, pp. 174-177.

(3) F. H. MacDougall, *THIS JOURNAL*, **38**, 528 (1916); **39**, 1229 (1917).

(4) S. F. Pickering, U. S. Bureau of Standards Circular No. 279 (1925).

first used by Dieterici⁵ in fitting experimental data at temperatures other than the critical. This form was also used by Porter in fitting the Joule-Thomson inversion curves of nitrogen and carbon dioxide⁶ and was found by him to give good correspondence with p - v - t data at moderate pressures.⁷

TABLE I

COMPARISON OF EQUATIONS OF STATE

	$RT_c/p_c v_c$	Boyle temp., T_c	Joule-T. max. invers. temp., T_c	$\left(\frac{T}{p} \frac{\partial p}{\partial T}\right)_{crit.}$
van der Waals eqn.	2.67	3.37	6.75	4
Eqn. (1)	3.69	4.00	8.00	3
Eqn. (2)	3.69	2.52	4.64	4
Eqn. (3)	3.69	2.52	4.64	6.2
Av. obs. value	3.7	2.5	~5	7

It can be seen from Table I, in which several tests are applied to equations of state, that equation (2) should be more successful than equation (1). However, with respect to the critical value of the pressure coefficient at constant volume, $T/p \partial p/\partial T$, equation (2) represents but a slight improvement on equation (1).

A further modification of Dieterici's equation is here proposed:

$$p = \frac{RT}{v-b} - \frac{R\sqrt{TT_c}}{v-b} (1 - e^{-a/vRT}) \quad (3)$$

The second virial coefficients in the virial expansions of equations (2) and (3) are identical, so that equation (3) reduces to equation (2) at low pressures and large volumes. At the critical temperature equation (3) like equation (2) reduces to equation (1). Equation (3), however, gives a value of 6.2 for the pressure coefficient at the critical point, close to the experimental value of 7 observed for non-polar substances, and may therefore be more satisfactory than equation (2) at higher pressures.

Since nitrogen is representative of the average behavior of non-polar gases,⁸ equations (1), (2) and (3) have been compared against smoothed compressibility data of this gas. In each case the volumes tabulated by Deming and Shupe⁹ for pressures of 20 to 100 atmospheres between -70 and 600° were used to calculate the pressures. The values of the constants a and b in all three equations were obtained from the critical temperature and pressure of nitrogen with the aid of the relationships $a = 4R^2T_c^2/p_c e^2$, $b = RT_c/p_c e^2$ in accordance with the usual procedure.¹⁰

Inspection of Table II shows that equation (3) gives better results than either equation (1) or (2), except for a restricted temperature interval

(5) C. Dieterici, *Ann. Physik*, **5**, 51 (1901).

(6) A. W. Porter, *Phil. Mag.*, **19**, 888 (1910).

(7) A. W. Porter in "Glazebrook's Dictionary of Applied Physics," The Macmillan Company, 1922, Vol. I, pp. 892-893.

(8) R. H. Newton, *Ind. Eng. Chem.*, **27**, 302 (1935).

(9) W. E. Deming and L. E. Shupe, *Phys. Rev.*, **37**, 638 (1931).

(10) B. F. Dodge, "Chemical Engineering Thermodynamics," McGraw-Hill Book Co., New York, N. Y., 1944, p. 179.