were easily separated from the residual, unreacted, insoluble rare earth fluorides.

Solubility.—The solubilities of the rare earth fluoroplatinates were determined approximately by measuring the least amount of water necessary to dissolve a weighed sample of the salt at a temperature of 30°.

Density.—The densities were determined at 30° with a 1-ml. pycnometer using toluene as the displacement liquid.

Absorption Spectra.—For each compound the absorption spectrum was measured with a model DU Beckman spectrophotometer using matched 1-cm. cells.

Analyses.—The compounds were analyzed according to the accepted analytical procedures. Each of the rare earth elements was determined by precipitation as the oxalate. After filtration of the precipitate, it was titrated with standard permanganate solution. Platinum was determined by reduction of the fluoroplatinate ion with hydrazine. Fluorine was determined gravimetrically as lead fluochloride. The results are summarized in Table I.

TABLE I

ANALYTICAL DATA

Compound	Rare earth, % Calcd.	Rare earth, % Found	Platinum, % Calcd.	Platinum, % Found	Fluoride, % Calcd.	Fluoride, % Found
$La_2(PtF_6)_3$	23.05	22.93	48.58	48.47	28.37	28.22
$Pr_2(PtF_6)_3$	23.30	23.16	48.43	48.12	28.27	28.01
$Nd_2(PtF_6)_3$	23.72	23.45	48.16	48.00	28.12	27.90

Discussion

The fluoroplatinate of cerium was the only one which could not be isolated. This was to be expected, since tetravalent cerium was produced by the action of fluorine. The addition of water to the cerium product resulted in the immediate but gradually complete hydrolysis of the salt. The addition of oxalic acid to a fresh solution of the cerium fluoroplatinate precipitated all of the cerium at once, leaving the fluoroplatinate ion in solution.

The presence of this ion was established by (a) its precipitation as potassium fluoroplatinate through the addition of potassium fluoride and (b) the subsequent analysis of this precipitate. The alkali fluoroplatinates will be the subject of a future paper.

The aqueous solution of lanthanum fluoroplatinate has a pale yellow color. Since lanthanum ions are colorless, this color may be attributed to the fluoroplatinate ion. The absorption spectrum of this compound revealed two characteristic peaks of the fluoroplatinate ion at 273 and 308 mμ. These appeared in all subsequent absorption spectra measurements of other fluoroplatinate compounds.

The color of praseodymium fluoroplatinate is yellow-green, whereas that of neodymium is lavender. In the absorption spectra of these two compounds, the bands characteristic of praseodymium and neodymium as well as those of the fluoroplatinate ions are evident.

The solubilities and densities of the rare earth fluoroplatinates are given in Table II.

TABLE II

Fluoroplatinates	Density	Solubility/100 g. of H_2O
Lanthanum	2.63	7.5
Praseodymium	2.64	7.1
Neodymium	2.66	6.6

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Kinetics of Chlorine Replacement by Ethylate Ion in Ethanol Solutions of Symmetrical Trichlorobenzene[1]

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Previous work on the replacement of aromatic halogen by basic ions indicates the reactions are of second order.[3-5]

Some of the above studies[6-12] involve aromatic compounds which are subject to reduction in anhydrous alcohol solution, particularly at temperatures greater than 70°.

In a preliminary study Holleman[13] showed that symmetrical 1,3,5-trichlorobenzene reacts reasonably rapidly with base in methanol solution without forming large amounts of phenols.

The present results are concerned with the replacement of halogen in 1,3,5-trichlorobenzene by ethylate ion in anhydrous ethanol.

The replacement process of halogen by ethylate on the benzene ring forms under certain conditions several reaction products two of which were identified. One was 3,5-dichlorophenetole (compound A of Table I) the other was 3,5-diethoxychlorobenzene (compound B of Table I).

These compounds were recovered from a relatively large amount of a reaction mixture consisting initially of excess sodium ethylate, 1,3,5-trichlorobenzene and anhydrous ethanol which was kept at 170° in a glass lined bomb for 50 hours under nitrogen. The amount of 3,5-diethoxychlorobenzene recovered was about 15% of the amount of

TABLE I

PROPERTIES OF THE REACTION PRODUCTS AND THEIR DERIVATIVES

		Compound A	3,5-Dichlorophenetole[a]	Compound B	3,5-Diethoxychlorobenzene[b]
B.p., °C. (mm.)		92 (4) 106 (8)	... ...	111 (4) 116 (8)	....
$n^{20}D$		1.5405	...	1.5225	....
Analysis, %	C	50.20 50.15	50.28	60.49 60.56	59.85
	H	4.88 4.52	4.22	6.71 6.82	6.53
Phenol dev., m.p., °C.		64.4–65.5	68	114.0–116.5	117
Benzoate dev., m.p., °C.		56.8–57.4	55	....	....
Hydrate dev.		....	...	Formed in moist benzene	Insoluble in benzene

[a] E. H. Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 217. [b] *Ibid.*, pp. 340.

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3,5-dichlorophenetole recovered. The properties of the 3,5-dichlorophenetole and 3,5-diethoxychlorobenzene and those of certain of their derivatives are summarized in Table I.

Similar experiments with solutions containing an excess 1,3,5-trichlorobenzene over sodium ethylate in ethanol yielded 3,5-dichlorophenetole only, in detectable amounts. Thus it would appear that the replacement process consists of stepwise reactions the first step being the reaction in which 3,5-dichlorophenetole was formed.

The kinetics for the first step replacement reaction at various temperatures are given in Table II. The rate constants were calculated under the assumption that the reaction is first order each in ethylate ion and in 1,3,5-trichlorobenzene. The constants at any one temperature agree to within 1% of one another even when the reaction was run to 90% completion.

TABLE II

SUMMARY OF KINETIC DATA

$T = 161.92 \pm 0.01,° \ d = 0.6312, \ a = 0.1043$

t, min.	H^+, ml.	k
0	10.44	
140	8.86	11.69
285	7.62	11.43
480	6.27	11.47
645	5.38	11.45
870	4.49	11.21
1201	3.33	11.60
1515	2.61	11.60

TABLE III

SUMMARY OF THE RESULTS

k_{cor} is the average k corrected for density changes of the alcohol. The average deviations are of the order of 1%.

Run	T, °C.	a, M	b, M	$k_{cor} \times 10^3$
I	149.42	0.1043	0.0522	5.37
II	161.92	.1043	.0522	14.3
III	169.6	.1000	.0464	26.6
IV	174.32	.1043	.0522	36.1
V	185.57	.1043	.0522	78.4
VI	186.69	.1043	.0522	85.4

The slope corresponding to $d \ln k_{cor}/d(1/T)$ for the first replacement reaction corresponds to an activation energy of 28,650 ± 300 cal./mole where k_{cor} is the rate constant and T is the absolute temperature.

The rate of halogen replacement of 1,3,5-trichlorobenzene by ethylate is about twice as fast as the similar replacement by methylate.[13]

No rearrangement products were found for this reaction in agreement with the work of Ogata and Okano[14] who studied aromatic ether interchange reactions.

Thus a mechanism which involves simple direct expulsion of chlorine from the aromatic compound by the incoming basic ion is consistent with the kinetic data of this work.[15]

Experimental

Preparation of Reactants.—1,3,5-Trichlorobenzene was prepared by deamination of 2,4,6-trichloroaniline by the method of Jackson and Lamar.[16] The 2,4,6-trichloroaniline was obtained from Eastman Kodak Company or for several samples prepared by the chlorination of aniline by the method of Chattaway and Irving.[17]

The purity of the 1,3,5-trichlorobenzene was determined in terms of a freezing point curve obtained with a platinum resistance thermometer. The freezing point obtained by calculating the freezing point depression when half the material had solidified was 62.79°. Assuming that the entropy of fusion is 5 cal. per degree mole, the amount of solid-insoluble, liquid-soluble impurity was 0.08 mole per cent. Commercial absolute ethyl alcohol was purified by a variation of the method of Danner and Hildebrand[18] using anhydrous oxalic acid instead of sulfuric acid. The alcohol was dried twice by the method of Smith[19] using diethyl phthalate and stored under pressurized nitrogen.

Sodium was prepared by pipetting clean molten C.P. sodium (Merck and Co.) under kerosene into test-tubes which were stored under dry kerosene. The sodium used to make sodium ethylate solutions was further purified by melting in vacuum and flowing it into glass tubes which were then sealed until used.

Apparatus.—The thermostat was a well-stirred, oil-filled 41-liter thermos bottle. The power delivered to the bath was controlled by a phase-shifting, proportional, electronic thermoregulator patterned after one by Tarnopol.[20] The thermostat when covered, could be maintained at a preset temperature to within 0.02°. The temperatures were measured by a platinum resistance thermometer which had been calibrated by the Bureau of Standards. The standard resistance thermometer used together with a Rubicon-Mueller Bridge gave temperatures accurate to 0.01°. The reaction tubes made of Pyrex glass, were of about 10-ml. capacity. Each tube was provided with a small neck which was sealed shut after the sample solution had been introduced.

A stock solution of sodium ethylate was made under dry, oxygen-free nitrogen from the dry ethyl alcohol and purified sodium. 1,3,5-Trichlorobenzene was accurately weighed into a tared volumetric flask, stock sodium ethylate solution was added and then enough dry alcohol to fill the flask to the mark. After mixing, approximately six milliliters of the solution was pipetted into each of several clean, dry tubes which were then sealed. All of the above procedure was performed under dry oxygen-free nitrogen. The sealed tubes were then placed in the thermostat at the appropriate temperature for a measured interval of time and then rapidly cooled in kerosene. The original solution and the solution from the sample tubes were titrated under nitrogen by pipetting samples from each solution into separate solutions containing a known amount of standard acid present in excess, and back titrating with a standardized barium hydroxide solution. All end-points were determined by means of a Beckman pH meter.

Calculations.—The second-order rate constant, k, was calculated from the relation

$$k = \frac{1}{t(b-a)} \ln \frac{a}{b} \frac{(b-x)}{(a-x)}$$

where t is the time in minutes, a and b are the initial concentrations of 1,3,5-trichlorobenzene and ethylate ion and x is the concentration in moles per liter of the products present at the time t. The rate constants are corrected for the thermal expansion of the solution, by using the temperature-density data for pure alcohol.

Identification of Products.—Both A and B were prepared by allowing excess ethylate to react with 1,3,5-trichlorobenzene for a long period of time. A typical reaction was carried out by mixing an alcoholic solution which was 0.50 M in sodium ethylate and 0.43 M in 1,3,5-trichlorobenzene. This mixture was kept for 50 hours at 170° in a glass-lined, stainless steel bomb. The total phenolic residues of this reaction were less than 0.7%. The actual 3,5-dichlorophenol present must have been far less than this, since its characteristic strong odor was not distinguishable. The two compounds were found to be aromatic ethers. They were separated by fractional distillation. Compound B was

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found to be present to the extent of about 10 to 20% of the amount of A formed.

The properties of 3,5-dichlorophenetole and 3,5-diethoxychlorobenzene, the expected products of the reaction, have not been previously given. For identification compounds A and B were cleaved with solid, anhydrous $AlCl_3$ to give the corresponding phenols. The benzoate of the phenol from compound A and the hydrate of the phenol from compound B were prepared. Table I summarizes the properties of compound A, compound B, 3,5-dichlorophenetole, 3,5-diethoxychlorobenzene and their indicated derivatives.

Since the carbon analyses for compound B are high it would appear that other products also were formed in small amounts; these were not identified. It seems clear that the compounds given are the major ones and the properties of 3,5-dichlorophenetole are fairly well defined.

Kinetic Results.—The kinetic studies data of the reaction are given in Table II where T is the temperature of the reaction in degrees centigrade, d is the density of alcohol at the temperature T, t is the time in minutes, ml. H^+ is the volume in milliliters of standard (0.02503 N) acid used in the titration, k is the calculated second-order rate constant in liter mole min.

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Absorption Spectra and Basicity of 2,3-Diaminodibenzofuran[1]

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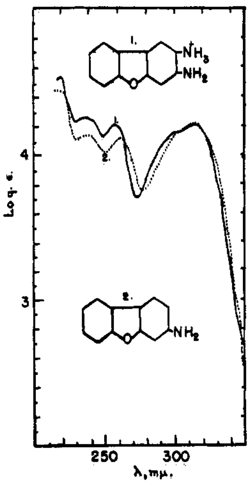
In connection with an extensive investigation in this Laboratory on the chemical and physical properties of the aromatic carcinogens, it was of interest to determine the basicity of 2,3-diaminodibenzofuran as compared to 3-aminodibenzofuran. In the latter compound the amino group is in the extended para position as it is in all the known biphenylene carcinogens.[2,3] In Fig. 1, the monoprotonated derivative of the diamine is shown to have a spectra similar to that of 3-aminodibenzofuran. This means that the 2-amino group in the diamine is the more basic group. This is not unexpected, for the resonance effect of the oxygen atom would have a base-strengthening effect on this group. Consistent with this is the fact that 3-aminodibenzofuran has a pK_a of 3.3 while the diamine has a pK_a of 4.1. The diprotonated derivative of 2,3-diaminodibenzofuran, Fig. 2, curve 1, and the protonated derivative of 3-aminodibenzofuran, Fig. 3, curve 1, are shown to be spectrally similar to dibenzofuran, Fig. 2, curve 2. Comparison of these spectra with that of the diamine in Fig. 3, curve 2, emphasizes the remarkable changes caused by salt formation. In Fig. 4 are shown the typical curves obtained in the determination of the dissociation constant.



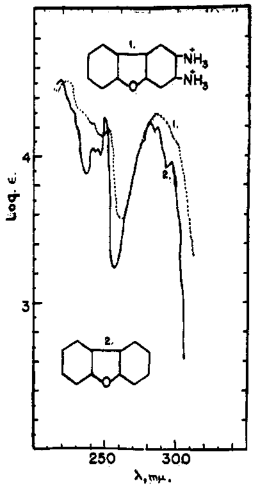
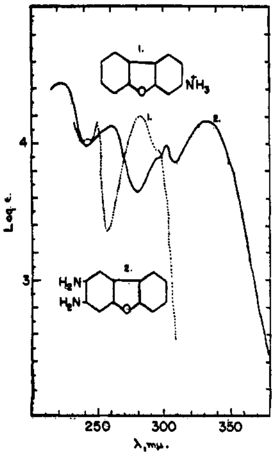


Fig. 1.—(1) 2,3-Diaminodibenzofuran in 50% ethanolic 0.08 N HCl; (2) 3-aminodibenzofuran in 95% ethanol.

Fig. 2.—(1) 2,3-Diaminodibenzofuran in 50% ethanolic 6 N HCl; (2) dibenzofuran in 95% ethanol.



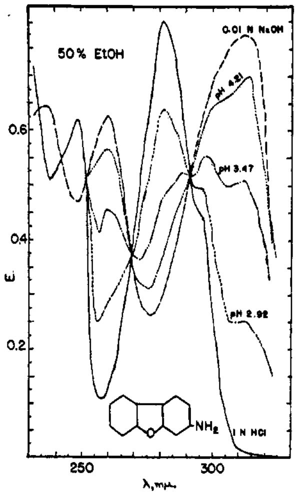


Fig. 3.—(1) 3-Aminodibenzofuran in 50% ethanolic 1 N HCl; (2) 2,3-diaminodibenzofuran in 95% ethanol.

Fig. 4.—3-Aminodibenzofuran in 50% ethanol.

Experimental

Dibenzofuran, m.p. 83–84°, gave an ultraviolet spectrum showing λ_{max} 218, 241, 244, 249, 280, 286 and 296 mμ and log ε 4.51, 4.04, 4.04, 4.26, 4.22, 4.19 and 3.95, respectively. Shoulders occurred at *ca.* 227, 275 and 300 mμ and log ε 4.31, 4.09 and 3.65. This agrees substantially with values reported in the literature.[4]

3-Aminodibenzofuran, m.p. 99°, was prepared by the procedure of Gilman and Avakian.[5] The ultraviolet spectrum showed λ_{max} 217–218, 237–238, 261 and 313 mμ and log ε 4.44, 4.13, 4.11 and 4.22, respectively. A shoulder occurred at 302–303 mμ and log ε 4.15.

2,3-Diaminodibenzofuran, m.p. 166°, was prepared by the procedure of Gilman, *et al.*[6] The ultraviolet spectrum showed λ_{max} 222–223, 259, 302 and 333 mμ and log ε 4.44, 4.12, 3.99 and 4.16, respectively. A shoulder occurred at 295–296 mμ and log ε 3.90.

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