uct was repeatedly washed with distilled water and dried at 110°. Samples from two different preparations were used in the chlorine determinations. *Anal.* Calcd. for $C_{20}H_{10}O_5I_2$: I, 43.46; Cl, 0.00. Found: I, 35.96, 36.15; Cl, 7.75, 7.80.

It is to be noted that the total determined halogen content indicates the occurrence of some tri- or tetrahalogenation.

Chlorination may have been due to chlorine released by the action of the excess dichloramine-T on chloride ion.[5] Although the presence of some chlorine in the product might be accounted for by adsorption of potassium chloride or dichloramine-T, this is unlikely, as approximately one-sixth of the weight of the product would have to consist of potassium chloride (or an even greater fraction of adsorbed dichloramine-T) to account for all the chlorine present.

It was not possible to prepare pure diiodofluorescein-I_2^{131} using the method[3] for 3,5-diiodo-4-pyridone-I_2^{131}.

Acknowledgment.—This work was supported in part by the Office of Naval Research, Contract No. N8onr 60500.

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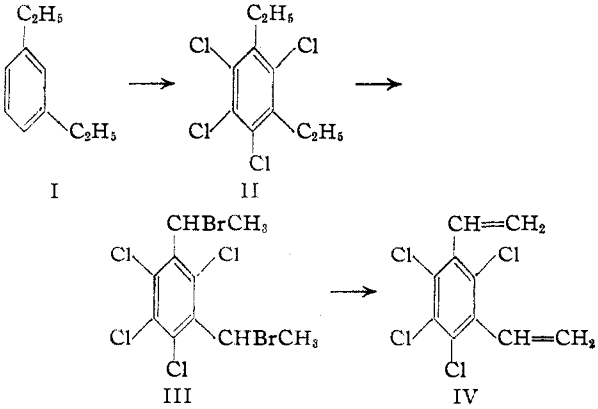
[5] R. A. Bradfield, K. J. P. Orton and I. C. Roberts, *J. Chem. Soc.*, 782 (1928).

RADIOISOTOPE LABORATORY AND
VENABLE CHEMICAL LABORATORY
UNIVERSITY OF NORTH CAROLINA
CHAPEL HILL, NORTH CAROLINA RECEIVED MARCH 2, 1951

The Preparation of 1,3-Divinyl-2,4,5,6-tetrachlorobenzene[1]

BY SIDNEY D. ROSS AND MOUSHY MARKARIAN

In a previous report from this Laboratory,[2] we described the preparation of 1,4-divinyl-2,3,5,6-tetrachlorobenzene and its copolymerization with styrene. It is our present purpose to report the preparation of 1,3-divinyl-2,4,5,6-tetrachlorobenzene by the sequence of reactions



Experimental

1,3-Diethyl-2,4,5,6-tetrachlorobenzene (II).—In a 1-liter 3-neck flask equipped with a thermometer, dropping funnel and reflux condenser were placed *m*-diethylbenzene (134 g., 1 mole), obtained from the Dow Chemical Company, and aluminum chloride (5 g.). From the dropping funnel the chlorinating mixture, consisting of sulfuryl chloride (544 g., and sulfur monochloride (5.44 g.), was added slowly, maintaining the temperature at 35–45°. When all of the chlorinating mixture had been added, the cooling bath was removed, and the reaction mixture was allowed to stand at room temperature overnight. Carbon tetrachloride was added, and the solution was decanted from the aluminum chloride complex, washed several times with water and finally dried over magnesium sulfate. The solvent was removed, and the residue was distilled at 11 mm. A mixture of liquid and crystals of b.p. 162–165.5° was obtained. The crystals were filtered and crystallized several times from ethanol to yield 42 g. (15%) of II of m.p. 41–43°.

Anal.[3] Calcd. for $C_{10}H_{10}Cl_4$: C, 43.73; H, 4.00. Found: C, 43.30, 43.44; H, 3.83, 3.76.

II has also been prepared by treating 1,2,3,5-tetrachlorobenzene with ethylene in the presence of aluminum chloride.[4] Most of the 1,3-diethyl-2,4,5,6-tetrachlorobenzene used in this work was obtained by crystallization of the mixed diethyltetrachlorobenzenes obtained from the Dow Chemical Company.

1,3-Bis-(α-bromoethyl)-2,4,5,6-tetrachlorobenzene (III).—Bromine (320 g., 2 moles) was added slowly to II (271.8 g., 1 mole) in carbon tetrachloride (3 liters). The solution was illuminated and maintained at the boiling point by a projection bulb inserted directly into the solution. Removal of the solvent gave 400 g. (92%) of the crude product of m.p. 61–70°. Recrystallization from ligroin (b.p. 90–100°) gave 224 g. (51.5%) of III, m.p. 95–99°. As in the case of the 1,4-isomer this product is undoubtedly a mixture of the *meso* and *dl*-forms.

Anal. Calcd. for $C_{10}H_8Cl_4Br_2$: C, 27.97; H, 1.86. Found: C, 27.70, 27.78; H, 1.70, 1.57.

1,3-Divinyl-2,4,5,6-tetrachlorobenzene (IV).—III (21.4 g., 0.05 mole) was refluxed one hour with sodium hydroxide (6 g., 0.15 mole) in ethanol (200 cc.) and then poured into water. Crystallization of the crude product from ethanol yielded 6.6 g. (47%) of IV, m.p. 53–55°.

Anal. Calcd. for $C_{10}H_6Cl_4$: C, 44.85; H, 2.26. Found: C, 44.90, 44.78; H, 2.53, 2.39.

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[1] This work was carried out under contract no. W36-039-sc-38110 with the Signal Corps of the United States Army.

[2] S. D. Ross, M. Markarian, H. H. Young, Jr., and M. Nazzewski, THIS JOURNAL, **72**, 1133 (1950).

[3] The microanalyses are by Dr. Carl Tiedcke.

[4] M. Istrati, *Ann. chim. phys.*, [6] **6**, 500 (1885).

RESEARCH LABORATORIES OF
THE SPRAGUE ELECTRIC COMPANY
NORTH ADAMS, MASSACHUSETTS RECEIVED MAY 8, 1951

Spectrophotometric Evidence for the Absence of Free Aldehyde Groups in Periodate-oxidized Cellulose[1]

BY JOHN W. ROWEN,[2] FLORENCE H. FORZIATI[2] AND RICHARD E. REEVES[3]

As a part of an investigation of the application of infrared spectrophotometry to a study of cotton cellulose, it was desired to locate the absorption produced by the C=O stretching vibration of aldehyde groups in oxidized celluloses. Periodate-oxidized cotton cellulose appeared to be a suitable material for the study of free aldehyde groups in cellulose inasmuch as the oxidized anhydroglucose unit is usually assumed to contain two free aldehyde groups as shown in structure I. An alternative structure, II, containing one free aldehyde and one hemiacetal group has also been proposed.[4] However, observations on periodate-oxidized cellulose

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[1] A report of work done under coöperative agreement with the United States Department of Agriculture and authorized by the Research and Marketing Act. The work is being supervised by the Southern Regional Research Laboratory of the Bureau of Agricultural and Industrial Chemistry.

[2] National Bureau of Standards.

[3] Southern Regional Research Laboratory.

[4] Mitchell and Purves, THIS JOURNAL, **64**, 589 (1942).

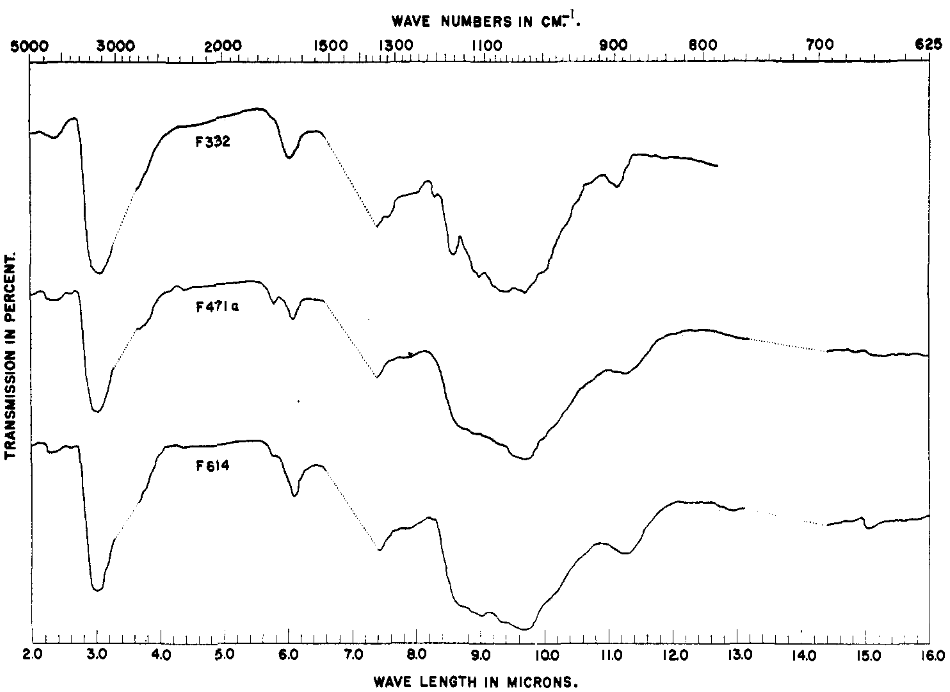
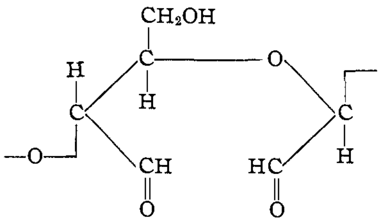
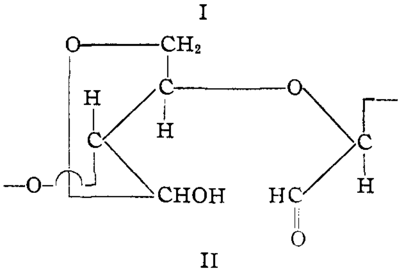


Fig. 1.—Infrared absorption spectra of mineral oil slurries of unoxidized cotton (F332); periodate-oxidized cotton in which 66% of the anhydroglucose units have been converted to dialdehyde (F471a); periodate-oxidized cotton in which 79% of the anhydroglucose units have been converted to dialdehyde (F614). All samples were ground to 200 mesh or finer. Dotted lines are shown in regions obscured by absorption of the mineral oil.

by numerous workers have failed to yield positive evidence substantiating either I or II.



I



II

Infrared absorption spectra were obtained with mineral oil slurries of five samples of periodate-oxidized cotton cellulose. In three of these samples, the percentage conversion of anhydroglucose units to dialdehyde was estimated from the amount of periodate consumed and found to be approximately 50, 66 and 79%. In the case of the 66% converted product, the percentage conversion was also calculated from the carbonyl content as determined by the hydroxylamine hydrochloride method[5] and found to be 60%. Spectra of the two most completely oxidized products and of the original cotton are shown in Fig. 1. These spectra show that periodate oxidation of cotton cellulose results in surprisingly little change in the region of the spectrum in which the intense absorption of the C=O stretching vibration occurs, the 5.5- to 6.5-micron region.[6,7] The weak band at 5.8 microns suggests the presence of only a very low concentration of carbonyl groups. Furthermore, since these oxidized celluloses probably contain small amounts of carboxyl and since the carboxylic carbonyl of oxidized celluloses has been shown to absorb at 5.8 microns,[8] the absorption of the periodate-oxidized cellulose at this wave length cannot be definitely attributed to aldehyde groups. The intensity of the absorption of the oxidized cellulose at 6.1 microns is approximately the same as that of the unoxidized cellulose. Inasmuch as the oxidized cellulose contains adsorbed water, it appears that the absorption at this wave length is largely attributable to adsorbed water in this material as well as in the original cellulose.[9,10] No absorption is found at 6.2 microns where Kuhn[11] found an intense band, which he attributed to aldehydic carbonyl, in the spectrum of the periodate-oxidation product of methyl α-D-glucoside. The results suggest either that the absorption of aldehydic carbonyl in periodate-oxidized cotton cellulose is of unusually low intensity or that few if any aldehyde groups as such are present. The change in the 8- to 10-micron re-

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[5] Gladding and Purves, *Paper Trade J.*, **116**, 150 (1943).

[6] Barnes, Gore, Liddel and Williams, "Infrared Spectroscopy," Reinhold Publishing Corp., New York, N. Y., 1944.

[7] Randall, Fowler, Fuson and Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1949.

[8] Forziati, Rowen and Plyler, *J. Research Natl. Bur. Standards*, **46**, 288 (1951), RP 2197.

[9] Forziati and Rowen, *ibid.*, **46**, 38 (1951), RP 2172.

[10] Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945.

[11] Kuhn, *Anal. Chem.*, **22**, 276 (1950).

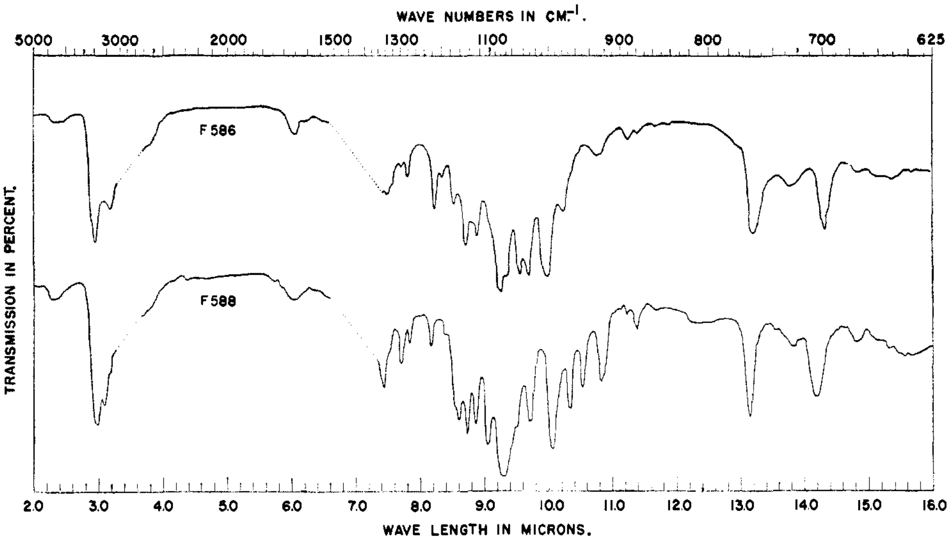
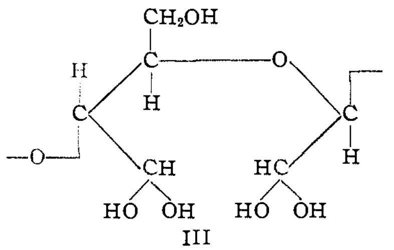


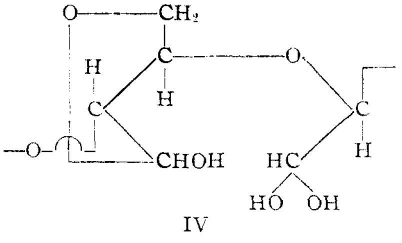
Fig. 2.—Infrared absorption spectra of mineral oil slurries of methyl 4,6-benzylidene-α-D-glucopyranoside (F586) and the dihydrate of its periodate-oxidation product (F588). Dotted lines are shown in regions obscured by the absorption of the mineral oil.

gion of the spectrum is probably caused in part by the cleavage of the anhydroglucose rings.

The absence of free aldehyde groups in periodate-oxidized cellulose might be explained by assuming that all of the aldehyde groups have reacted with residual alcohol groups to form hemiacetal groups. This explanation is considered an unlikely one, however, for in the highly oxidized celluloses the number of alcohol groups available is too small to tie up all of the aldehyde groups. A more likely explanation is that at least one and possibly both of the aldehyde groups of the oxidized anhydroglucose units shown in I or II have reacted with water, forming either III or IV.



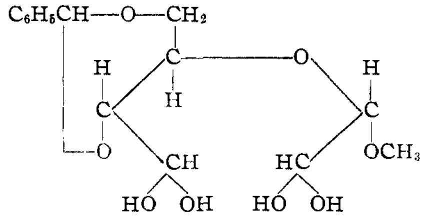
III



IV

This type of hydrated carbonyl has been suggested by Malaprade[12] as an intermediate in the periodate oxidation of adjacent hydroxyl and carbonyl groups. Neither hydrated aldehyde nor hemiacetal groups would be expected to show the absorption characteristics of free aldehyde groups. The hydroxyl groups of hydrated aldehyde and hemiacetal groups would presumably contribute to the absorption of the OH stretching vibration at approximately 3 microns. Chemically, hydrated aldehyde groups would be expected to resemble hemiacetal and free aldehyde groups.

This explanation for the absence of free aldehyde groups in periodate-oxidized cellulose is further supported by observations on the absorption spectrum of the crystalline dihydrate of the periodate oxidation product of methyl 4,6-benzylidene-α-D-glucopyranoside. This oxidation product has not been previously reported and is therefore described in the final paragraph of this note. Infrared absorption spectra of mineral oil slurries of methyl 4,6-benzylidene-α-D-glucopyranoside and the dihydrate of its periodate oxidation product are given in Fig. 2. The absence of intense absorption in the 5.5- to 6.5-micron region of the spectrum of the periodate oxidation product indicates that little, if any, free aldehyde is present. Since this oxidation product contains neither primary nor secondary alcohol groups, the only logical explanation for the absence of free aldehyde groups is that the aldehyde groups are hydrated as shown in V.



V

The absorption at approximately 3 microns is attributed to the hydroxyls of the hydrated aldehyde groups.

Experimental

Periodate Oxidation of Methyl 4,6-Benzylidene-α-D-glucopyranoside.—The oxidation of 114.2 mg. of methyl 4,6-benzylidene-α-D-glucopyranoside dissolved in 100 ml. of 0.0312 molar periodate and buffered to *p*H 8 consumed 0.93 mole of oxidant per mole of glucoside in 42 hours at 25°. Crystals separated from the solution during the reaction

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(12) Malaprade, *Bull. soc. chim.*, [5] 1, 831 (1934).

and were removed by filtration, yield 24 mg. The product was obtained in almost quantitative yield in a second experiment in which the reaction mixture was cooled after the oxidation had gone to completion. After drying in vacuum, the crystals melted, not sharply, at about 135–145° and gave analyses in agreement with the dihydrate of the expected oxidation product.

Anal. Calcd. for $C_{14}H_{16}O_6 \cdot 2H_2O$ (316.3): C, 53.16; H, 6.37. Found: C, 52.55, 52.69; H, 6.36, 6.26.

The crystals were insoluble in cold alcohol, cold acetone and hot or cold chloroform. Recrystallization did not occur from warm alcohol, but occurred slowly when water was added to the solution obtained by boiling with acetone.

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WASHINGTON 25, D. C. AND
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NEW ORLEANS 19, LOUISIANA RECEIVED FEBRUARY 2, 1951

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[13] Inquiries concerning this paper should be addressed to Dr. Florence H. Forziati, National Bureau of Standards, Washington 25, D. C.

[14] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

Oxygen Atom Transfer in Oxidation–Reduction Reactions. II. The Mechanism of the Sulfite–Nitrite Reaction

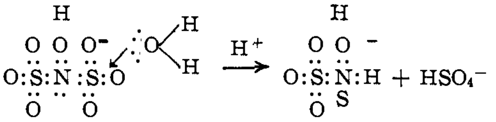
BY AARON C. RUTENBERG, JOSEPH HALPERIN[1] AND HENRY TAUBE

In an earlier communication,[2] the possibility was suggested that some oxyoxidizing agents in water may act by removing electrons from the reducing agent, the oxygen added to the reducing agent being supplied by the solvent. Consideration of the facts known about the reactions of nitrite and sulfite leads to the conclusion that the mechanism of oxidation of sulfite by nitrite is almost certainly of this type. Among others, the net changes 1 and 2 take place in the system

$$2H^+ + NO_2^- + 2SO_3^= + H_2O = NH_3OH^+ + 2SO_4^= \quad (1)$$

$$2H^+ + NO_2^- + 3SO_3^= + H_2O = NH_4^+ + 3SO_4^= \quad (2)$$

Under appropriate conditions compounds containing the complexes hydroxylamine disulfonate ($HON(SO_3)_2^=$) and amine trisulfonate ($N(SO_3)_3^{\equiv}$) can be isolated from the reaction mixture in good yield. On hydrolysis in acid solution, the former ion yields NH_3OH^+ and $SO_4^=$, and the latter yields NH_4^+ and $SO_4^=$. These complexes can therefore be regarded as intermediates for the net changes 1 and 2 above. It seems reasonable, although this has not been proven, that the "nitrite" and "sulfite" radicals in the complexes are joined by N–S bonds. The formation of $SO_4^=$ from hydroxylamine disulfonate, for example, may therefore be considered to take place in the following way.



It is clear from this formulation that each product sulfate will contain one oxygen atom derived from the solvent.

To point up this electron transfer mechanism for the action of nitrite on sulfite, the compounds $(KSO_3)_2NOH$ and $(KSO_3)_3N \cdot 2H_2O$ were prepared, and hydrolyzed by acid in water differing in oxygen isotope composition from that of the compounds. Isotopic analysis of the product sulfate showed that it contained one (and only one) oxygen atom per $SO_4^=$ derived from the solvent. The experiments remove any doubt as to the role the solvent plays as a source of oxygen in the present system. They prove furthermore that the "sulfite" bound in the complexes does not exchange oxygen with the solvent. This strengthens the formulations of the complexes as being internally joined by N–S bonds, and shows also that the complexes are not in rapid equilibrium with sulfite as a dissociation product. Sulfite in acid is known to exchange very rapidly with the solvent under the conditions of the hydrolysis.[3]

Experimental

Anhydrous $(K_2SO_3)_2NOH$ was prepared by the method of Naiditch and Yost.[4] Owing to its instability, the compound was used immediately after being prepared. $(KSO_3)_3N \cdot 2H_2O$ was prepared as described by Sisler and Audrieth.[5]

Table I gives an account of the experimental conditions, and presents the results obtained. The method used for the isotopic analysis of the product sulfate will be described in a future communication.[3]

TABLE I

OXYGEN TRANSFER IN THE HYDROLYSIS OF HYDROXYLAMINE DISULFONATE AND AMINE TRISULFONATE

N represents the mole fraction of O^{18}; the subscripts o, h and p designate, respectively, the water used in the hydrolysis, the complex salt and the product sulfate. Temp. *ca.* 25°.

Salt	Salt concn., *M*	(HCl) *M*	$N_o \times 10^3$	$N_h \times 10^3$	$N_p \times 10^3$	No. of O from solvent in each SO_4
$(KSO_3)_2NOH$	0.46[a]	0.235	15.625	2.130	5.254	0.93 ± 0.05
$(KSO_3)_2NOH$	.78[a]	.235	15.625	2.130	5.127	.89 ± .05
$(KSO_3)_2NOH$	.37[a]	*ca.* .5	15.500	2.130	5.311	.96 ± .05
$(KSO_3)_3N \cdot 2H_2O$	.24[b]	.11	15.006	2.130	5.161	.95 ± .05
$(KSO_3)_3N \cdot 2H_2O$	.18[c]	.69	15.737	2.130	5.368	.94 ± .05

[a] 1.0 mole $SO_4^=$ formed per mole of salt. [b] 2.0 moles $SO_4^=$ formed per mole of salt. [c] 1.7 moles $SO_4^=$ formed per mole of salt.

The systematic deviation from unity of the values for transfer from the solvent may be attributed in part to isotope fractionation. It is in the direction expected for H_2O^{16} reacting in the hydrolysis more rapidly than does H_2O^{18}.

Acknowledgment.—This research was supported by the Office of Naval Research under contract N6-ori-02026. The funds for the purchase of the

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[1] A.E.C. Pre-doctoral Fellow.

[2] J. Halperin and H. Taube, THIS JOURNAL, **72**, 3319 (1950).

[3] J. Halperin and H. Taube, in preparation for publication.

[4] S. Naiditch and D. M. Yost, THIS JOURNAL, **63**, 2123 (1941).

[5] H. Sisler and L. F. Audrieth, *ibid.*, **60**, 1947 (1938).