

basis of the electrophoresis data thus far obtained. It seems probable that they are caused by the changes of the salt and protein gradients superimposed on any given boundary in the mixture. The proportionality of the relative concentration of albumin to the total protein as shown in Fig. 3 is in agreement with the assumption made by Longsworth for superimposed salt gradients.<sup>11</sup>

A similar relationship might perhaps be found for all the variations observed. The results thus indicate that as the ratio of the concentration of protein to that of salt is decreased the relative concentrations, as determined from the ratios of pattern areas, approach their true values. For purposes of accuracy it appears preferable to increase the ionic strength of the buffer medium rather than to reduce the protein concentration as has been pointed out by Svensson.<sup>4</sup> The patterns obtained at low salt concentration (Fig. 2) indicate a different type of phenomenon. An interaction of proteins, usually disregarded in electrophoretic analysis, does exist and becomes apparent with small variations in experimental conditions. It is obvious from the anomalies shown in Fig. 2 that in a mixture, one protein must influence the transference of another protein and therefore affect the electrophoretic separation of components.

(11) Compare footnote on page 336 in reference (3) and Roberts and Kirkwood, *THIS JOURNAL*, **63**, 1373 (1941).

**Acknowledgment.**—We wish to thank Dr. L. G. Longsworth of the Rockefeller Institute for his kind interest and advice which have been of great value throughout our electrophoretic work. We are also indebted to Dr. J. L. Oncley of the Department of Physical Chemistry, Harvard Medical School.

### Summary

The effect of ionic strength and protein concentration on the apparent distribution of the components in the electrophoretic analysis of normal human plasma was investigated. A sodium diethylbarbiturate buffer of pH 8.6 was used.

In a 2% protein solution the apparent concentration of albumin decreased from 57 to 54% and the  $\gamma$ -globulin rose from 10 to 13% when the ionic strength was increased from 0.1 to 0.3.

When the ionic strength of the buffer was kept constant and the protein concentration varied, changes of the same order of magnitude were found.

The results indicate that the ratio of the concentration of protein to that of salt influences the apparent distribution of proteins in an electrophoretic diagram. On decrease of this ratio true values for the relative concentrations are approached.

BOSTON, MASSACHUSETTS RECEIVED JANUARY 2, 1945

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

## Reaction of Methylene Chloride and other Halide Vapors with Sodium

BY ALFRED SAFFER<sup>1</sup> AND T. W. DAVIS

A study of the reaction of alkyl iodides with metallic sodium<sup>2</sup> at temperatures in the neighborhood of 300° led to a consideration of hydrogen-transfer reactions of the type  $\text{CH}_2\text{X} + \text{—R} \rightarrow \text{RH} + \text{—CH}_2\text{X}$ , where  $\text{—R}$  is an alkyl free radical and X is a halogen atom. It was suggested that some of the  $\text{—CH}_2\text{X}$  radicals would form dihalides, e. g.,  $\text{CH}_2\text{X}_2$ , by picking up halogen from the original reactant.<sup>3</sup> These dihalides should themselves enter Wurtz-type reactions and, indeed, Bawn and Milstead<sup>4</sup> have found that the treatment of methylene and ethylene dihalides with sodium vapor gives practically 100% ethylene when nitrogen is the carrier gas and nearly 100% methane or ethane when hydrogen is the carrier. The experiments of Bawn and Milstead were carried out by the dilute flame method under such conditions that the initial reactions were certainly in the gas phase. But despite the clarity

and directness of these experiments, we have undertaken a further study of the reaction of sodium with dihalides under conditions more closely resembling those in our earlier investigation and we find totally different products from those reported by Bawn and Milstead.

**Procedure.**—The procedures employed were essentially identical with those used earlier.<sup>2</sup> The organic halide vapors were allowed to bubble through an excess of sodium liquid either continuously or in batches and the products were removed by a Toepler pump, condensed and separated by isothermal evaporation. Material volatile at  $-196^\circ$ ,  $-131^\circ$  and  $-78^\circ$  was removed successively and analyzed in an Orsat type apparatus.

Unreacted sodium was destroyed by methyl alcohol and the "black residues" insoluble in the alcohol were removed by filtration, washed, dried, weighed and analyzed. Sodium chloride was determined by Volhard analysis.

The batch addition of halide vapor was accomplished in two different ways and the composition of the products depended on which of the two

(1) Present address: Frick Chemical Laboratory, Princeton University, Princeton, N. J.

(2) Saffer and Davis, *THIS JOURNAL*, **64**, 2039 (1942).

(3) West and Schlessinger, *ibid.*, **60**, 961 (1938).

(4) Bawn and Milstead, *Trans. Faraday Soc.*, **35**, 889 (1938).

methods was used. The first, called the "liquid addition" method consisted of allowing slugs of dihalide liquid to fall on a hot surface where the material was flashed into vapor before passing through the molten sodium. This method did not permit careful control of the reactant pressures. After enough liquid had been admitted to bring the pressure to a desired level, reaction was allowed to take place for about ten minutes before the products were removed. During the time the vapors remained in contact with the sodium, liquid often continued to leak by the stopcock, building up the pressure to as much as an atmosphere. Better control was achieved by the "vapor-addition" method whereby the dihalide was drawn as vapor from a storage bulb of the reactant. Most of the experiments were conducted in the latter way, some batchwise and some continuously.

The halides used in this work were commercial products dried over calcium chloride, redistilled and carefully degassed before use. The boiling points and refractive indices checked closely the values appearing in the literature.

**Results.**—A summary of results from the methylene chloride runs appears below.

Two important facts may be noted at once. First, the composition of the gases is nearly independent of the experimental details of pressure, temperature, presence of glass packing, and time of treatment and, second, the products which include large amounts of elemental hydrogen and carbon and practically none of the expected Wurtz product, ethylene, can be accounted for only on the basis of free radical reactions.

The reaction leading to the formation of carbon occurs on the surface of the liquid sodium and not

TABLE I  
PRODUCTS FROM REACTION OF METHYLENE CHLORIDE WITH SODIUM

Temp., °C.	260	320	320	320	320	320	320
Method <sup>a</sup>	C	A	A	A <sup>d</sup>	B	B <sup>e</sup>	B <sup>e</sup>
Initial press., mm.	2-3	~350	~350	~350	313	~300	~310
Reaction time, hours	5	6.5	4	4.3	1	0.9	1
H <sub>2</sub> in gases, %	38	18	19	17	32	38	34
CH <sub>4</sub> in gases, %	54	76	74	76	57	51	57
C <sub>2</sub> H <sub>2</sub> in gases, %	0.6	0.4	0.5	0.6	1	1	1
C <sub>2</sub> H <sub>4</sub> in gases, %	5	2	3	4	6	6	4
C <sub>2</sub> H <sub>6</sub> in gases, %	2	4	3	2	4	4	4
Total gas (S. T. P.), ml.	77.4	568.8	725.3	285.3	162.9	145.3	142.5
Black res., mg.	98.1	569.5	713.4	c	112.0	c	c
% C in black res.	52.6	73.6	75.7	c	59.2	c	c
% H in black res.	4.0	3.6	4.0	c	2.2	c	c
CH <sub>2</sub> Cl <sub>2</sub> used, ml.	3.4	9.6	9.6	9.6	1.3	1	1
NaCl formed, g.	0.994	7.470	9.713	c	1.760	c	c
% Reaction	15.9	42.3	55.0	c	73.4	c	c
% C recovered	80	90	88	c	76	c	c
% H recovered <sup>b</sup>	81	81	80	c	87	c	c

<sup>a</sup> Method A = batch addition of liquid, B = batch addition of vapor, C = continuous flow of vapor. <sup>b</sup> Based on the assumption that the difference between 100% and the sum of carbon, hydrogen and ash in the black residue is oxygen present as water. <sup>c</sup> Not determined. <sup>d</sup> Vessel packed with glass tubing. <sup>e</sup> This experiment was carried out in two parts, without the usual removal of sodium between the two runs.

320	320	320	320	320	320	320	370	370	370
B	B	B	C	C	C	C	C	C	C
170	75	75	2	6	6	~30	3-6	4-6	6-8
1.5	0.1	0.1	4	3	3	0.3	3	3	3
38	37	41	40	41	36	31	43	42	43
51	47	44	50	50	52	57	50	50	51
1	2	2	0.8	0.8	0.7	1	0.5	0.5	0.4
5	11	11	7	6	9	9	6	6	5
5	3	2	2	2	2	2	1	1	1
149.7	117.0	126.5	73.3	169.3	170.0	186.8	86.0	141.9	137.6
92.1	62.6	61.6	110.2	159.1	c	134.6	81.5	110.4	c
59.9	69.6	69.4	40.5	51.0	c	58.4	50.6	58.4	c
2.2	2.4	2.6	2.4	2.0	c	2.5	2.8	2.2	c
1.1	1.8	1.4	0.5	1.3	1.1	3.5	0.5	0.9	1.0
1.509	1.160	1.184	0.706	1.710	c	1.949	0.760	1.295	c
74.3	34.9	45.9	76.7	71.6	c	30.2	82.8	78.4	c
76	79	76	103	82	c	80	100	87	c
85	86	90	75	83	c	85	93	109	c

in the gas phase and it may be that all the important reactions occur there as well. Were carbon formed as a gas, it would either condense on all the surfaces in the reaction bulb, or as clouds of soot. It did neither; rather it was found entirely in the excess sodium at the conclusion of the reactions. The black product seems to be carbon although in rather impure state. It is entirely insoluble in ether, acetone, ethyl alcohol, ligroin and tetralin. It contains hydrogen and also an insoluble silicate residue which is unavoidably introduced by corrosion of the glass vessel when the unused sodium is destroyed by alcohol and water. The hydrogen in the sample was probably present as adsorbed water and in all except five of the micro-analyses of black residues the carbon, water and silicate added up to 100% within two or three per cent. when the hydrogen was considered to be present only as water. Carbon prepared by dehydrating sugar seems to have about an equivalent water-retaining capacity. In the five experiments where the assumption that hydrogen was present only as water gave analyses exceeding 100%, the excess hydrogen was included in the materials-balance.

The incomplete recovery of both carbon and hydrogen in the reaction products led us to pass the gases evolved during the destruction of one of the sodium residues into ammoniacal silver nitrate solution. A precipitate of silver acetylide was noted and it suggests that a portion of the carbon may form sodium carbide. The unreacted methylene chloride after some of the runs was distilled. No evidence of higher molecular weight products was found although it must be said that the method would not reveal small quantities of such products.

To check on the possibility of secondary reactions occurring between sodium and the hydrocarbon gases formed in the system, samples of several of the product gases were passed through the system under a variety of conditions. Ethylene, propylene, methane and ethane were not affected by sodium at 320° beyond a possible formation of traces of hydrogen from the two unsaturated gases. Acetylene, however, reacts slowly. It does not polymerize at 320° either in the presence or absence of sodium,<sup>5</sup> but it does produce methane, ethylene, ethane, carbon and hydrogen. The results from two experiments appear in Table II.

There is rather little hydrogenation of the acetylene on the sodium surface but there is a considerable amount of breaking of C-C bonds to give methane and a considerable amount of dehydrogenation to give carbon. The principal reaction, of course, is liberation of hydrogen and formation presumably of sodium acetylide. One might consider that a molecule of acetylene adsorbed on a sodium surface would resemble a free methylene radical on the surface of sodium. Both

TABLE II

PRODUCTS FROM ACETYLENE-SODIUM REACTION  
Temp., 320°; press., 100 mm.; total contact time, 80 min.

% H <sub>2</sub> in gases	84	86
% CH <sub>4</sub> in gases	4	3
% C <sub>2</sub> H <sub>4</sub> in gases	8	8
% C <sub>2</sub> H <sub>6</sub> in gases	4	3
Vol. gaseous product, ml.	87.6	76.8
Vol. C <sub>2</sub> H <sub>2</sub> added, ml.	124	120
Vol. C <sub>2</sub> H <sub>2</sub> unreacted, ml.	19.6	28.9
% Reaction	85	75
Black Residue, mg.	11.8	78
% Hydrogen recovered	100.3	99.6
% Carbon recovered	22.3	19.5

are unsaturated and should enter into the same kinds of reaction. To some extent they do. There is a much greater tendency of the acetylene, however, to release hydrogen and to produce gases with two carbon atoms per molecule rather than methane. It is a striking feature of the results that even as much as 10% of the acetylene residues on the sodium rearrange to form carbon even though the configuration must already be close to that of sodium acetylide. That 10% of the reaction gives hydrogenated products, ethylene, ethane and methane, is striking as well, for sodium is not a hydrogenation catalyst.<sup>6</sup>

The observations on acetylene and sodium can be compared with the results of chloroform-sodium reactions as recorded below.

TABLE III

REACTION PRODUCTS FROM CHLOROFORM AND SODIUM AT 320° AT A PRESSURE OF 170 MM.

CHCl <sub>3</sub> used, g.	1.8	2.1	3.3
Reaction time, hr.	1.5	1.3	3.0
H <sub>2</sub> in gases, %	77	68	73
CH <sub>4</sub> in gases, %	21	29	25
C <sub>2</sub> H <sub>2</sub> in gases, %	0.1	0.3	0.2
C <sub>2</sub> H <sub>4</sub> in gases, %	0.5	0.3	0.7
C <sub>2</sub> H <sub>6</sub> in gases, %	2	2	1
Total gases produced, ml.	74.4	62.2	100.7
Black residue, mg.	167.3	..	287.4
NaCl formed, g.	2.177	..	3.723
% Reaction	83	..	77

Over 98% of the carbon goes into the black residue. The yield of the Wurtz product, acetylene, is close to zero. The recovery of hydrogen is rather poor in these experiments, namely, 70% in one and 60% in the other, perhaps as a result of formation of hydrocarbons which remain adsorbed on the carbon surface.

**Mechanism of the Reactions.**—The multiplicity of products from the reactions and the circumstances of their formation suggest a series of free radical reactions following the preliminary formation of CH<sub>2</sub> groups from methylene chloride, and CH from chloroform. Contrary to the impression created by the ordinary formulation of

(5) Taylor and van Hook, *J. Phys. Chem.*, **39**, 811 (1935).

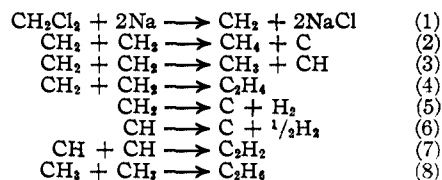
(6) O. Schmidt, *Chem. Rev.*, **12**, 363 (1933).

the Wurtz reactions, the union of the free radicals to give stable products does not occur with high efficiency as compared with alternative possibilities. Indeed a direct measurement by Allen and Bawn<sup>7</sup> showed that methyls do not largely combine after a few collisions in the gas phase<sup>8</sup> and measurements of the half life of alkyl radicals in gaseous flow systems show a unimolecular disappearance,<sup>9</sup> which is expected if the disappearance is a wall reaction. On the wall, these radicals do seem largely to combine, but in a way that may be a function of the surface. While Paneth and Lautsch observed that ethyl radicals disappear about equally fast in the presence of iron, glass or quartz, it is not known that the same products are formed in each case. On the other hand, the influence of neighboring groups in determining the behavior of particular atoms in compounds is well known in organic chemistry and the specific character of catalytic surfaces in promoting particular reactions is equally well known.<sup>10</sup> That free radicals give different products depending on the nature and temperature of the adsorbing surfaces is entirely to be expected, for each of the adsorbates is essentially a distinct chemical species.

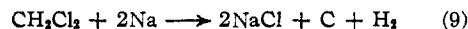
The results of our experiments are in agreement with the work of Turkevich and Taylor<sup>11</sup> and may be understood in terms of the theory of activated or chemisorption developed to explain phenomena in the field of catalysis. Turkevich and Taylor observed in an even lower temperature range than in our work that the lighter hydrocarbon gases are adsorbed on manganese-chromium oxide and on copper catalysts partly in an activated state. This type of adsorption like more familiar chemical processes requires an activation energy. The velocity of the activated adsorption depends on the activation energy, which in turn is a function of the catalytic surface and the adsorbed material. When a hydrocarbon suffers activated adsorption, it may undergo a variety of reactions, including breaking and reunion of bonds such as occurs in our own experiments. Turkevich and Taylor found the reactions to amount to an exchange of hydrogen between reacting species including complete hydrogenation to methane and complete dehydrogenation to carbon with accompanying fission of C—C linkages.

Radicals from the reaction of sodium with organic polyhalides appear to be chemisorbed on the excess sodium and in this condition they behave much as do the stable hydrocarbons on special catalysts and they behave exactly as do the radicals from alkyl halides adsorbed on sodium. On the other hand, at 320°, the hydro-

carbons do not undergo chemisorption, on sodium, except acetylene, to some extent, presumably because the activation energies are too large. It is not possible to write satisfactory equations for the behavior of the adsorbed radicals in the activated state but the following summarize the over-all effects, each of the reactions occurring in the adsorbed layer



These equations should not be taken as showing anything beyond stoichiometric relations. The first reaction is written to show the removal of two Cl's per molecule inasmuch as  $\text{CH}_2\text{Cl}$  is probably unstable.<sup>12</sup> A primary reaction leading to the appearance of carbon and hydrogen, that is



would be endothermic and so is not apt to be important on that account. Moreover, it is not probable that the energy would be so localized as to lead often to this particular distribution of products. The copious production of carbon and hydrogen in the  $\text{CH}_3\text{I} + \text{Na}$  and  $\text{C}_2\text{H}_5\text{I} + \text{Na}$  reactions in the same temperature range suggests a common source, namely, secondary reactions between the radicals.

As compared with the hydrogen exchange reactions, combination reactions (4), (7) and (8) seem to be inefficient processes on the metal surface. The unlike radicals do not combine, presumably, because they would do so in two stages, the primary product being an unstable radical of short life even on the surface of molten sodium. A possible exception to this latter statement may be provided by  $\text{CH}_3\text{CH}$  unions to give ethylene, for Bawn and Milstead found that ethylidene chloride and sodium vapor give a high yield of ethylene, the ethylidene radical rearranging easily to give the corresponding alkene. We have observed also that, in our apparatus, ethylidene chloride reacts with sodium to give a fairly high yield of ethylene.

An unusual feature of the present results is that chemisorption occurs on a liquid rather than on a solid surface. While it is possible to imagine the active spots of a solid catalyst to arise from the unsaturation associated with surfaces, edges and points, it would appear that if chemisorption occurs on a liquid, it should occur at every point in the surface. Since the surface of the liquid can be purged by stirring, liquid contact catalysts should be especially efficient in promoting reactions where non-volatile products result. Little work on molten liquid catalysts has been reported

(7) Allen and Bawn, *Trans. Faraday Soc.*, **34**, 463 (1938).  
 (8) Cf. also Davis, Jahn and Burton, *THIS JOURNAL*, **60**, 10 (1938).  
 (9) Paneth and Lautsch, *Ber.*, **64**, 2708 (1931); Pearson, *J. Chem. Soc.*, 1718 (1934); May, Taylor and Burton, *THIS JOURNAL*, **63**, 249 (1941); Feldman, Ricci and Burton, *J. Chem. Phys.*, **10**, 618 (1942).  
 (10) Schwab, Taylor and Spence, "Catalysis," D. Van Nostrand Co., Inc., New York, N. Y., 1937, p. 263.  
 (11) Turkevich and Taylor, *THIS JOURNAL*, **56**, 2254 (1934).

(12) Cf. Gregory and Style, *Trans. Faraday Soc.*, **32**, 724 (1936).

in the literature, but Steacie and Elkin<sup>13</sup> have observed that lead above the melting point is even more active in promoting the decomposition of methyl alcohol than solid lead of equal gross surface area. Hartman and Brown<sup>14</sup> found also that the catalytic efficiency of cadmium in reduction of nitrobenzene is little affected by melting.

In our own experiments, there is the possibility of reactions between the adsorbate and substances in the vapor phase. When the pressure of reactant halide approaches one atmosphere, the mechanism may include such additional reactions as  $\text{CH}_2 + \text{CH}_2\text{Cl}_2 (\text{g}) \xrightarrow{(\text{Na})} \text{CH}_4 + \text{C} + \text{NaCl}$ . This reaction accounts stoichiometrically for a reduction in the production of hydrogen and an increase in the production of methane at higher pressures of halide.

On metals, other than sodium, chemisorption of aliphatic free radicals seems to have been observed by other authors. For example, in the presence of reduced nickel, a metal which normally promotes hydrogenation, the decomposition products from a mixture of hydrogen and methylene chloride at 200° are carbon and hydrogen chloride.<sup>15</sup> Chloroform and hydrogen give the same products.

(13) Steacie and Elkin, *Proc. Roy. Soc. (London)*, **142A**, 457 (1933); *Can. J. Res.*, **11**, 47 (1934).

(14) Hartman and Brown, *J. Phys. Chem.*, **34**, 2651 (1930).

(15) Sabatier and Mailhe, *Compt. rend.*, **138**, 408 (1904).

Tollens<sup>16</sup> identified hydrogen, acetylene, ethylene, ethane and chloroethylene in products from the reaction of ethylidene chloride and sodium in the temperature range 180–200°. We have found the products at 320° to be carbon, hydrogen and methane as well as the C<sub>2</sub> gases. A similar difference is found when chloroform is the reactant. At 320°, the CH radicals resulting from the initial chloroform and sodium reaction are adsorbed in an activated state. The most important stable products are carbon and hydrogen. At lower temperatures, chloroform and potassium amalgam are a source of acetylene,<sup>17</sup> as are chloroform and copper.<sup>18</sup> The effect of temperature on the equilibria at the surface would account for the different proportions of products.

### Summary

Carbon, hydrogen and methane with smaller amounts of ethane, ethylene and acetylene are the principal products formed by passing methylene chloride or chloroform into molten sodium over a fairly wide range of temperatures and pressures.

A series of reactions between free radicals adsorbed in an activated state on the surface of the metal is suggested as source of the products.

(16) Tollens, *Ann.*, **137**, 311 (1866).

(17) Beilstein, "Handbuch der organischen Chemie," 4th edition, J. Springer, Berlin, 1918, vol. 1, p. 60.

(18) Berthelot, *Compt. rend.*, **50**, 805 (1860).

NEW YORK, N. Y.

RECEIVED OCTOBER 16, 1944

[CONTRIBUTION FROM THE INSTITUTE OF PAPER CHEMISTRY]

## Acetic Acid Spruce Lignin and Acetic Acid Willstätter Spruce Lignin<sup>1</sup>

By F. E. BRAUNS AND M. A. BUCHANAN

Lignin can be extracted from wood by organic acids in the presence of small amounts of mineral acid as a catalyst. In 1916, Pauly<sup>2</sup> described the delignification of wood by means of acetic acid in the presence of sulfuric acid and in 1921 Pauly and Foulon<sup>3</sup> isolated lignin with 85% acetic acid containing 0.3% sulfuric acid. Routala and Sevón<sup>4</sup> reported in 1927 that glacial acetic acid containing a trace of hydrochloric acid dissolved at least a part of the lignin which they isolated by pouring the acetic acid solution into water. The lignin had a methoxyl content of 14.6%. A year later, Friedrich<sup>5</sup> isolated lignin in a similar way, but the lignin, after purification from alcohol and water, had a methoxyl content of only 10.5%, from which it was concluded that considerable acetylation had taken place. After saponifica-

tion with sodium hydroxide and purification of the crude lignin by dissolving it in chloroform and reprecipitating it with ether, a lignin with 14.4 to 14.6% methoxyl was obtained.

Schütz and Knackstedt<sup>6</sup> recently described the extraction of lignin from wood by means of acetic acid with magnesium chloride as a catalyst. This mixture was used also by Freudenberg and Plankenhorn<sup>7</sup> who claimed that, by repeated extraction, almost the entire lignin can be brought into solution and that the various fractions do not differ in their chemical composition. The acetic acid lignin obtained by Freudenberg had a methoxyl content of 13.2% and an acetyl content of 10.2%, corresponding to 2 acetyl groups per lignin building unit.<sup>8</sup> After saponification, the methoxyl increased to 14.6%. On treatment with 72% sulfuric acid, Freudenberg's acetic acid lignin lost 21.2% in weight, of which 10.2% was due to acetyl groups split off and 11% to solubility of carbohydrate material. The methoxyl content of

(1) This paper was presented at the New York, N. Y., meeting of The American Chemical Society, September 11, 1944.

(2) Pauly and Aktiengesellschaft für Zellstoff u. Papierfabrikation, German Patent 309,551 (June 20, 1916).

(3) Pauly, Foulon, *et al.*, *Ber.*, **67**, 1177 (1934).

(4) Routala and Sevón, *Ann. Acad. Sci. Fennicae*, **29A**, No. 11, 48 (1927).

(5) Friedrich, *Z. physiol. Chem.*, **176**, 127 (1928).

(6) Schütz and Knackstedt, *Cellulosechem.*, **20**, 15 (1942).

(7) Freudenberg and Plankenhorn, *Ber.*, **75**, 857 (1942).

(8) Brauns, *THIS JOURNAL*, **61**, 2120 (1939).