ide. After drying with "Drierite," the ether solution was saturated with dry hydrogen chloride, the aniline salt filtered off, and the ether evaporated. A small amount of nitrile was obtained in this manner when the reaction had been carried out at 97–100°.

Blanks were run with β-3,4-methylenedioxybenzaldoxime in solutions of *n*-butylamine and pyridine; the oxime was recovered unchanged from these solutions.

The products from the reactions of acetyl-β-aldoxime (1–2 g. samples) with 50 cc. of 1 *M* solutions of amine in water and in dry dioxane were isolated as follows: after standing several days at 0 or 30°, the solids were filtered off from the aqueous mixtures, and the oxime separated from nitrile by means of alkali; in certain cases additional oxime was obtained from the aqueous amine filtrate. The dioxane solutions were evaporated to dryness in an air-draft, and the residue treated with alkali. In the reactions with aqueous and alcoholic ammonia, oxime and nitrile were isolated in a similar manner.

It has been found also that certain other acetyl-β-aldoximes with aniline give only the corresponding oxime; the yields of this product from acetyl-β-benzaldoxime and acetyl-β-3-nitrobenzaldoxime were 85 and 99%, respectively.

Summary

1. A study has been made of the reactions of acetyl-α- and acetyl-β-3,4-methylenedioxybenzaldoximes with certain primary, secondary and tertiary amines.

2. It has been found that when the acetyl-α-aldoxime is dissolved in the primary or secondary amines it is converted to the corresponding aldoxime; this reaction appears to be quantitative. The acetyl-α-aldoxime, however, is stable in the presence of the tertiary amines under ordinary conditions.

3. The acetyl-β-aldoxime reacts with the tertiary amines to form only nitrile, but, in general, with primary and secondary amines to form both nitrile and β-aldoxime, the yields of these products depending upon the temperature of reaction and apparently upon the basic strength of the amine used.

DURHAM, N. C. RECEIVED JUNE 10, 1936

[COMMUNICATION NO. 591 FROM THE KODAK RESEARCH LABORATORIES]

The Alkaline Decomposition of Cellulose Nitrate. I. Quantitative Studies[1]

BY W. O. KENYON AND H. LEB. GRAY

Previous workers have shown that the action of alkalies, especially potassium or sodium hydroxides, on aliphatic nitrates is not one of simple saponification regenerating the alcohol and forming sodium nitrate, but is a profound decomposition yielding also sodium nitrite and oxidation products of the aliphatic group. Thus, alkyl nitrates[2–5] give rise to ethers, alcohols, inorganic nitrates and nitrites, aldehydes and resinous bodies when treated with alkalies. Ethylene dinitrate[3,4,6] is stated to yield carbon dioxide, oxalic acid and glycol. The products of the alkaline decomposition of glycerol trinitrate[3,7–13] are stated to include: ammonia, carbon dioxide, formic acid, acetic acid, oxalic acid, mesoxalic acid, alkali cyanides, alkali nitrates, alkali nitrites and intermediate peroxides. The presence of glycerol is affirmed[13] and denied.[7] From nitrated mannose,[8] the formation of nitrates, nitrites, oxalic acid and unidentified organic acids is reported. Glucose,[14–16] levulose and starch trinitrates are said to yield products from which the osazones of oxypyruvic acid or its homologs may be isolated. Partially denitrated carbohydrates were also found.

The products reported by various authors as formed by the alkaline decomposition of cellulose nitrate are naturally greater in number and more complex. These include inorganic nitrates and nitrites,[17,18] ammonia,[18] cyanide,[19] carbon dioxide,[20] oxalic,[17,21,8] malic,[21] glycolic,[21] trioxy-

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(1) The material contained in this paper comprises a portion of a thesis presented by William O. Kenyon to the University of Rochester in partial fulfilment of the degree of Doctor of Philosophy, 1935.

(2) Berthelot, *Ann. chim. phys.*, **53**, 447 (1860).

(3) Mixter, *Am. Chem. J.*, **13**, 507 (1891).

(4) Millon, *Ann. chim. phys.*, [3] **8**. 233 (1845).

(5) Nef, *Ann.*, **309**, 126 (1899).

(6) Henry, *Ann. chim. phys.*, [4] **27**, 243 (1872).

(7) Hay, *Moni. Sci.*, [3] **27**, 424 (1885).

(8) Hay, *Trans. Roy. Soc. Edinburgh*, **32**, 67 (1885).

(9) Berthelot, *Compt. rend.*, **131**, 519 (1900).

(10) Berthelot, *Chem. Ind.*, **19**, 1038 (1900).

(11) Klason and Carlson, *Ber.*, **39**, 2752 (1906).

(12) Berl and Delpy, *ibid.*, **43**, 1421 (1910).

(13) Railton, *J. Chem. Soc.*, **7**, 222 (1855).

(14) Berl and Smith, *Ber.*, **41**, 1837 (1908).

(15) Berl and Smith, *J. Soc. Chem. Ind.*, **27**, 534 (1908).

(16) Berl and Smith, *Moni. Sci.*, [4] **23**, 51 (1909).

(17) Hadow, *J. Chem. Soc.*, **7**, 201 (1855).

(18) Béchamp, *Compt. rend.*, **41**, 817 (1855).

(19) Will, *Ber.*, **24**, 400 (1891).

(20) Vohl, *Dinglers polytech. J.*, **112**, 236 (1849).

(21) Berl and Fodor, *Z. ges. Schiess- Sprengstoffw.*, **5**, 296 (1910).

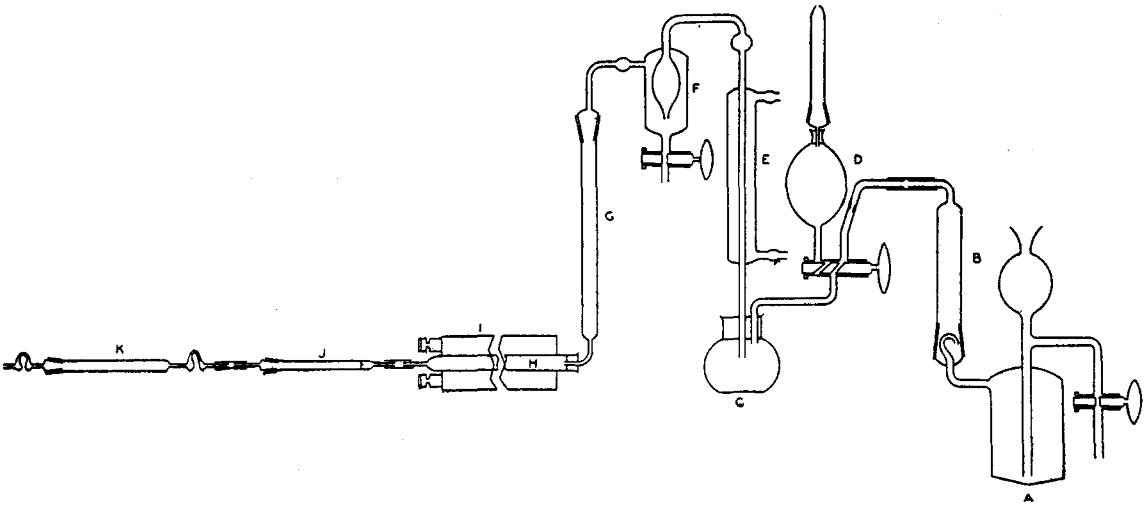

Fig. 1.

glutaric,[21] dioxybutyric,[21] malonic,[21] and tartronic acids,[21] sugars,[18,22] modified celluloses[18] and their nitrates,[23] and partially denitrated cellulose nitrates.[24,22,25] Unidentified complex acids are described.[17,26]

From the products of alkaline decomposition an osazone has been isolated which corresponds to the osazone of oxypyruvic acid.[14,15,16,19,21] Since this osazone may arise from several organic acids, attempts have been made to identify the acid present. One author[27] presents evidence for the presence of oxypyruvic acid (so-called keto form) while others believe the acid to be the semialdehyde of tartronic acid (aldehyde form).[28]

Quantitative studies of this reaction are more or less fragmentary. The formation of nitrites by the action of alkali on alkyl nitrates and the nitrates of ethylene glycol, glycerol, erythritol, mannitol, dulcitol and cellulose has been quantitatively measured.[29–31] Measurements of decomposition of various cellulose nitrates have been made by determination of the alkali consumed.[32,33]

Since no extended studies of the quantitative decomposition of cellulose nitrate could be found, we have studied in a quantitative manner the effect of certain variables: alkali concentration, ratio of alkali to ester, time, temperature and degree of nitration of the cellulose.

Experimental

A. General Procedures.—The cellulose nitrate was dried and 10-g. samples weighed to the nearest centigram (±0.1%). These were placed in flasks of suitable size with the amount of water which would yield the desired final concentration of alkali when the calculated amount of standard alkali was added. The water used in all of these experiments was freshly boiled, distilled water containing no amount of carbon dioxide capable of affecting the subsequent analyses.

The standard alkali used in all of these determinations possessed the following analysis: 0.77724 g. of sodium hydroxide per cc. at 25°; 0.007738 g. of sodium carbonate per cc. at 25°. The alkali concentrations given in this paper are expressed as grams of alkali per 100 cc. of water, *i. e.*, 20% = 20 g. per 100 cc. of water.

The aqueous suspensions of the cellulose nitrate were placed in a large water-bath and allowed to come to equilibrium with the temperature of the bath. The alkali was then quickly added with shaking to ensure complete mixing. The flasks were closed with rubber stoppers and placed in the bath until the decomposition was complete as evidenced by the disappearance of the suspended cellulose nitrate. During the reaction, the color of the liquid became reddish-brown. The temperature and total volume of the solutions were measured and the volume calculated to 25°, which was the temperature used for measurements of aliquots for analyses. Portions of the solutions were removed at various intervals, cooled to 25° and aliquots taken for the following measurements: (1) carbon dioxide, (2) optical rotation, (3) nitrites, (4) reducing power. The methods used for making these measurements were as follows.

(1) **Carbon Dioxide.**—Since we have been unable to find volatile organic acids other than carbon dioxide in the products of decomposition, the following method was adopted.

The apparatus used, Fig. 1, is an adaptation of that described by Kemmerer and Hallett.[34] It consists of a

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(22) Béchamp, *Bull. soc. chim.*, **3**, 289 (1863).

(23) Berl and Fodor, *Z. ges. Schiess- Sprengstoffw.*, **5**, 254 (1910).

(24) Béchamp, *Ann. chim. phys.*, **46**, 338 (1856).

(25) Eder, *Ber.*, **13**, 169 (1880).

(26) Schönbein, *Ann. chim. phys.*, **52**, 290 (1833).

(27) Aberson, *Z. physik. Chem.*, **31**, 17 (1899).

(28) Neuberg and Silbermann, *Z. physiol. Chem.*, **44**, 134 (1905).

(29) Vignon and Bay, *Compt. rend.*, **135**, 507 (1902).

(30) Carlson, *Arkiv. Kemi. Mineral. Geol.*, **3**, Art. 8, 1-15.

(31) Carlson, *Ber.*, **40**, 4191 (1907).

(32) Silberrad and Farmer, *J. Chem. Soc.*, **89**, 1759 (1906).

(33) Piest, *Z. angew. Chem.*, **23**, 1009 (1910).

(34) Kemmerer and Hallett, *Ind. Eng. Chem.*, **19**, 1352 (1927).

bulb A containing sulfuric acid which acts as a drying chamber for the incoming air as well as a bubble counter. The tube B contains Ascarite to remove carbon dioxide from the air. C is a 100-cc. Pyrex extraction flask in which the sample is placed and D is a dropping funnel to introduce the acid. This is closed by a stopper carrying another Ascarite tube. The evolved gases pass through the condenser E, the bubble counter F containing sulfuric acid and the drying tower G containing Dehydrite. The silica tube H is 35.5 cm. long, the portion within the furnace I being filled with a mixture of lead dioxide and shredded asbestos maintained at 180°. After the gases have passed through this tube, water is absorbed in the phosphorus pentoxide tube J and the dry carbon dioxide absorbed in the tube K, Ascarite being the absorbing medium.

The determination is made by connecting the source of vacuum to the drying tube J by means of the stopcock which serves to regulate the flow of gas through the apparatus. The carefully measured sample is placed in C and enough carbon dioxide-free distilled water added to bring the volume to 10 cc. The flask is replaced and the outfit swept out by passing air through it for one-half hour at a rate of about 100 bubbles per minute. The Ascarite tube K is then placed in the train and the rate of bubbling reduced to about 20–30 per minute. An excess of 5% sulfuric acid solution (boiled to expel carbon dioxide) is added from the dropping funnel (50–100 drops). The contents of the evolution flask are then heated to boiling with a micro burner and boiled for two minutes. The burner is removed and the apparatus swept out at the same rate for one-half hour. The tube K is removed and weighed.

In order to test the accuracy of the method, a series of determinations was made using varying amounts of a standard sodium carbonate solution (4.385 mg. of carbon dioxide per cc. by titration) and a solution containing sodium nitrate and sodium nitrite made up by accurately weighing the pure sodium salts. This latter solution contained 0.075 mole of sodium nitrite per liter and 0.025 mole of sodium nitrate per liter, this composition being approximately that shown by nitrite analyses to be present in the alkaline decomposition mixture. The results are tabulated in Table I.

TABLE I

Na_2CO_3 soln., cc.	Na_2CO_3, mg.	Nitrate–nitrite soln., cc.	$NaNO_2$, mg.	$NaNO_3$, mg.	Na_2CO_3 found, mg.
1	4.385	..	....	....	4.397
1	4.385	..	....	....	4.391
2	8.770	..	....	....	8.775
4	17.540	..	....	....	17.602
1	4.385	2	10.351	4.250	4.368
1	4.385	4	20.702	8.500	4.396
1	4.385	4	20.702	8.500	4.3875
1	4.385	8	41.404	17.000	4.374
1	4.385	12	62.106	25.500	4.428

It will be seen that good agreement was obtained in all cases. The runs containing 4 cc. of the nitrate–nitrite solutions correspond closely to the greatest nitrate–nitrite concentration encountered in the experiments and even a three-fold excess (12 cc.) had little effect on the determinations.

The carbonate determinations on the decomposition solutions are corrected for the amount of carbonate present in the alkali used.

(2) **Nitrite Determinations.**—The method employed was an adaptation of the procedure of Green and Rideal[35] in which the aniline solution used by them was replaced by a solution of sodium sulfanilate.

(3) **Reducing Power.**—The procedure used in these determinations was the modified method of Bertrand.[36] Using the relationships established experimentally by Bertrand for the reducing power of glucose, we have expressed the total reducing power of the alkaline decomposition solution in terms of glucose. This will be a fairly accurate measure of the moles of reducing substance present assuming one actual or potential aldehyde group for each molecule of reducing substance present.

(4) **Optical Rotation.**—Due to the brown color of the solutions, they were diluted before measuring the rotatory power. The desired amount of the alkaline solution was measured from a buret into a 10-cc. volumetric flask and diluted to 10 cc. The rotation was measured in a Hilger–Lippich half-shade polarimeter using light from a mercury arc lamp which was filtered to give a wave length of 546.1 mμ. A tube length of 0.5 dm. was used in each case. The measurements with this instrument are accurate to ±0.01°.

In each of the various determinations, the results are calculated on the basis of the total amount of solution produced in each experiment. Since the same amount of cellulose nitrate was used in each case, the results are, therefore, expressed on the basis of the same weight of cellulose nitrate.

B. Decomposition at 30°. Constant Ratio of Alkali to Cellulose Nitrate (12.2% *N*). Varying Alkali Concentrations.—The data for the solutions used in this series of experiments are given in Table II. Under the heading "Time of Decomposition" are given the times required for disappearance of the cellulose nitrate. The exact time of disappearance is difficult to judge but the values given represent, at least, the relative order of magnitude.

TABLE II

No.	Cellulose nitrate, g.	NaOH soln., cc.	NaOH concn., %	Time of dec., hrs.
1	10	100	20	2.58
2	10	200	10	11.13
3	10	400	5	23.33
4	10	800	2.5	170.9
5	10	2000	1.0	245.0

Samples were withdrawn from the solutions at various times and analyzed. Samples from solution 1 are designated as 1A to 1D inclusive, those from solution 2 as 2A to 2D inclusive, etc. The results are tabulated in Table III.

Under the heading "Time of Sampling" are given the intervals elapsed between the addition of the alkali and the withdrawal of samples for analyses.

C. Decomposition at 60°. Constant Ratio of Alkali to Cellulose Nitrate (12.2% *N*). Varying Alkali Concentrations.—This set of experiments was run at 60°, all other conditions as shown in Table IV being the same as in B.

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(35) Green and Rideal, *Chem. News*, **49**, 173 (1884).

(36) Bertrand, *Bull. soc. chim.*, **35**, 1285 (1906).

TABLE III

No.	Time of sampling, hrs.	CO_2 moles ($\times 10^{-3}$)	Moles CO_2 per mole cellulose nitrate	Nitrite moles ($\times 10^{-2}$)	Conversion to nitrite, %	Glucose equiv. moles ($\times 10^{-3}$)	Glucose equiv. moles per mole cellulose nitrate	Optical rotation degrees
1A	2,57	7.17	0.191	5.75	66.05	5.95	0.159	−1.2
1B	14.40	8.012	.214	5.58	64.20	4.41	.118	−1.6
1C	30.73	8.877	.237	5.75	66.05	3.43	.092	−1.5
1D	292.0	10.639	.284	5.75	66.05	1.82	.049	−1.6
2A	12.97	8.987	.239	5.89	67.70	6.39	.170	−0.5
2B	28.80	9.472	.252	6.05	69.55	6.11	.163	− .5
2C	51.30	9.818	.262	5.80	66.65	4.40	.114	− .75
2D	603.3	10.918	.291	5.97	68.80	3.65	.097	− .75
3A	23.33	8.420	.225	5.39	61.95	6.05	.162	− .30
3B	48.33	8.956	.239	5.68	65.25	5.61	.150	− .375
3C	196.83	10.087	.269	5.86	67.35	5.32	.142	− .375
3D	609.83	12.384	.330	5.84	67.10	2.67	.071	− .375
4A	170.88	11.594	.309	5.96	68.50	3.48	.093	− .18
4B	218.88	12.065	.322	5.96	68.50	3.48	.093	− .18
4C	360.88	13.119	.349	5.98	68.80	2.44	.065	− .19
4D	627.4	14.868	.397	6.00	68.95	2.22	.059	− .18
5A	245.0	10.491	.279	5.60	64.40	5.37	.143	− .06
5B	315.5	10.911	.291	5.66	65.00	4.40	.117	− .06
5C	585.0	13.388	.357	5.66	65.00	3.31	.088	− .06
5D	651.0	14.254	.380	5.65	64.95	3.02	.081	− .06

TABLE IV

No.	Cellulose nitrate, g.	NaOH soln., cc.	NaOH concn., %	Time of dec., hrs.
6	10	100	20	0.05
7	10	200	10	0.23
8	10	400	5	0.83
9	10	800	2.5	8.0

The results are tabulated in Table V.

D. Decomposition at 60°. Constant Concentration. Varying Ratio of Alkali to Cellulose Nitrate (12.2% *N*).—The data for the solutions used in this series of experiments are given in Table VI. The time of decomposition of the cellulose nitrate was about one hour in each case.

Samples were removed from each solution after 1104 hours (forty-six days) and analyzed. The results are tabulated in Table VII.

TABLE V

No.	Time of sampling, hrs.	CO_2 moles ($\times 10^{-3}$)	Moles CO_2 per mole cellulose nitrate	Nitrite moles ($\times 10^{-2}$)	Conversion to nitrite %	Glucose equiv. moles ($\times 10^{-3}$)	Glucose equiv. moles per mole cellulose nitrate	Optical rotation degrees
6A	19.70	11.246	0.300	6.17	70.92	1.18	0.0315	−1.10
6B	67.53	11.718	.312	6.17	70.92	1.05	.028	−1.10
6C	117.2	12.200	.326	6.09	70.00	0.76	.0203	−1.10
6D	1053.2	16.749	.447	6.02	69.19	.28	.0074	−1.10
7A	21.37	13.599	.362	6.22	71.50	1.43	.0381	−0.90
7B	70.62	14.630	.390	6.32	72.64	1.24	.0331	− .60
7C	144.13	15.699	.418	6.32	72.64	0.73	.0194	− .60
7D	1080.13	19.906	.531	6.32	72.64	.52	.0138	− .60
8A	23.33	15.456	.412	6.10	70.12	1.64	.0437	− .30
8B	72.92	15.977	.426	6.10	70.12	1.22	.0325	− .325
8C	145.83	17.448	.465	6.25	71.84	1.13	.0301	− .30
8D	1151.10	19.964	.532	6.22	71.50	1.03	.0275	− .275
9A	25.25	14.492	.386	6.16	70.80	1.96	.0523	− .175
9B	78.33	15.904	.424	6.14	70.57	1.73	.0461	− .15
9C	150.42	16.656	.444	6.14	70.57	1.68	.0448	− .15
9D	1153.16	18,537	.494	6.02	69.19	1.27	.0339	− .1375

TABLE VI

No.	Cellulose nitrate, g.	NaOH soln., cc.	NaOH concn., %	Ratio NaOH to cellulose nitrate (mole)
10	10	100	5.0	3.33
11	10	200	5.0	6.66
12	10	400	5.0	13.32
13	10	800	5.0	26.64
14	10	1600	5.0	53.28

Sample 10 was acid to litmus after decomposition and had the odor of oxides of nitrogen.

E. Decomposition at 60°. Constant Ratio of Alkali to Cellulose Nitrate (9.34% *N*). Varying Alkali Concentrations.—As shown in Table VIII this series of experiments was run under the same conditions as C except that a cellulose nitrate of lower nitrogen content was used. The times of decomposition were approximately the same as in C.

TABLE VII

No.	CO_2 moles ($\times 10^{-3}$)	Moles CO_2 per mole cellulose nitrate	Nitrite moles ($\times 10^{-2}$)	Conversion to nitrite, %	Glucose equiv. moles ($\times 10^{-3}$)	Glucose equiv. moles per mole cellulose nitrate	Optical rotation degrees
10	18.70	0.499	4.94	56.82	2.43	0.0648	−8.0
11	18.05	.481	6.26	71.95	1.10	.0293	−0.90
12	20.54	.548	7.16	82.26	1.01	.0269	− .375
13	15.65	.417	6.22	71.77	0.94	.0251	− .20
14	13.12	.350	6.28	72.24	0.85	.0226	− .00

TABLE VIII

No.	Cellulose nitrate, g.	NaOH soln., cc.	NaOH concn., %
15	10	100	20.0
16	10	200	10.0
17	10	400	5.0
18	10	800	2.5
19	10	2000	1.0

Samples were removed from each solution after 116 hours and analyzed. The results are tabulated in Table IX.

TABLE IX

No.	CO_2 moles ($\times 10^{-3}$)	Moles CO_2 per mole cellulose nitrate	Nitrite moles ($\times 10^{-2}$)	Conversion to nitrite %	Glucose equiv. moles ($\times 10^{-3}$)	Glucose equiv. moles per mole cellulose nitrate	Optical rotation degrees
15	9.15	0.213	3.33	49.93	0.561	0.0131	−2.20
16	9.24	.215	2.63	39.43	.742	.0173	−1.45
17	9.41	.219	3.18	47.68	.967	.0225	−0.60
18	9.68	.225	3.15	47.21	2.100	.0489	− .35
19	10.14	.236	3.02	45.28	4.250	.0990	− .14

Attempts were made to investigate quantitatively the alkaline decomposition of cellulose nitrates containing 5.0 and 1.2% of nitrogen. Neither of these decomposed to yield completely water soluble products even when heated for twenty-four hours on the steam-bath in the presence of 20% alkali.

Discussion

Cellulose nitrate, when decomposed by aqueous sodium hydroxide solutions, yields alkali soluble products among which are carbon dioxide and substances capable of reducing alkaline copper solutions. This oxidative decomposition of the cellulose molecule is accompanied by reduction of the nitrate groups to nitrite groups. The time required to decompose a given weight of cellulose nitrate decreases with increasing temperature and alkali concentration but appears independent of the alkali–cellulose nitrate ratio at constant concentration.

The amount of carbon dioxide formed at 30° from cellulose nitrate containing 12.2% *N* (Table III) varied between 0.191 and 0.397 mole per mole of cellulose nitrate, which is equivalent to about 3 to 6% by weight of the cellulose nitrate used. About 60 to 70% of the nitrate groups present were reduced to nitrite. When the solutions were allowed to stand, the amount of carbon dioxide increased and the reducing power decreased.

At 60°, the same cellulose nitrate (Table V) yielded larger amounts of carbon dioxide at the same alkali concentrations, the values increasing with time. The conversion of nitrate to nitrite was about 70 to 72%. The reducing powers of the solutions produced at 60° were decidedly lower than those formed at 30°. The initial reducing powers of the solution were greater when lower concentrations of alkali were used but in each case decreased with increasing reaction time.

The values for carbon dioxide and nitrite conversion, at constant concentration and varying alkali/cellulose nitrate ratio (Table VII), appear to pass through a maximum. The reducing powers of the solutions decreased with increasing alkali ratio.

Experiments at 60° with cellulose nitrate containing 9.34% nitrogen (Table IX) indicated that the amount of carbon dioxide produced increased with decreasing alkali concentration. The conversion of nitrate to nitrite (39–50%) was less than when cellulose nitrate containing 12.2% nitrogen was used. The reducing power of the solutions increased with decreasing concentrations of alkali.

Summary

The decomposition of cellulose nitrates in aqueous sodium hydroxide has been studied in a quantitative manner.

A relatively small amount of carbon dioxide is produced and a relatively large percentage of the nitrate groups is reduced to nitrite.

The production of carbon dioxide and of reducing substances appears to be related to time, concentration of alkali, ratio of alkali to cellulose nitrate and the temperature.

ROCHESTER, N. Y. RECEIVED MAY 6, 1936

[CONTRIBUTION NO. 265 FROM THE INDUSTRIAL FARM PRODUCTS RESEARCH DIVISION, BUREAU OF CHEMISTRY AND SOILS, UNITED STATES DEPARTMENT OF AGRICULTURE]

The Magenta Series. II. Some Higher Basic Members

BY JOHN T. SCANLAN

In a previous publication[1] the results of an investigation of the "nitrobenzene process" and the "formaldehyde process" for the preparation of Magenta (Fuchsine) were given. In the latter process 4,4′-diaminodiphenylmethane, or one of its homologs, reacts with aniline or its homologs, and it was shown that the reaction involves a scission of the diphenylmethane. This report covers an extension of the same investigation to three of the higher members of the series in which the methyl groups are ortho to the amino groups and not more than two occur in any benzene nucleus. The simplified system of nomenclature explained in the previous publication is used (see Table I).

TABLE I

NOMENCLATURE

Name used in this paper	Scientific name
Magenta IV	3,3′,3″,5-Tetramethyl-4,4′-diaminofuchsonimonium chloride
Magenta V	3,3′,3″5,5′-Pentamethyl-4,4′-diaminofuchsonimonium chloride
Magenta VI	3,3′,3″,5,5′,5″-Hexamethyl-4,4′-diaminofuchsonimonium chloride

The results are even more clean-cut than those obtained with the lower homologs and confirm the conclusions previously stated. As shown by the data in Table II and the corresponding absorption curves in Fig. 1, when 4,4′-diamino-3,3′-dimethyldiphenylmethane reacts with *v*-*m*-xylidine (Experiments 5Fa and 5Fb) the product is not Magenta IV but Magenta V and when 4,4′-diamino-3,3′,5,5′-tetramethyldiphenylmethane reacts with *o*-toluidine (Experiment 6F) the product is not Magenta V, but Magenta IV. This conclusion is readily arrived at by comparing the products of the above two reactions with that of the reaction between *as*-*m*-xylidine and *v*-*m*-xylidine (Experiment 6N, "nitrobenzene process") which must obviously be Magenta V. No attempt was made to prepare Magenta IV and Magenta VI by the "nitrobenzene process" because a necessary intermediate, mesidine, was not readily available and it was thought that further evidence was not required.

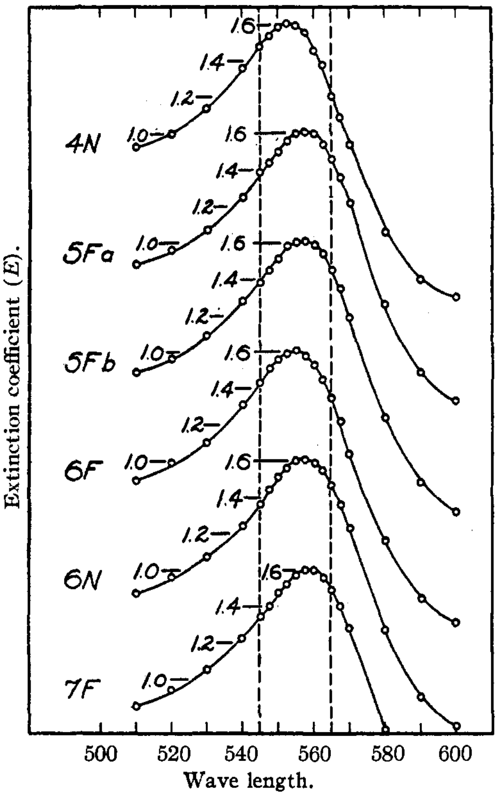

Fig. 1.—Absorption curves of the products obtained in the experiments indicated by the numbers. Solvent, 50% alcohol. The dyes corresponding to the curves are as follows: 4N, magenta III (repeated from previous paper for comparison); 6F, magenta IV; 5Fa, 5Fb and 6N, magenta V; 7F, magenta VI. Further data are given in Table II.

As in the case of the lower homologs, the solubility of these dyes (hydrochlorides) in alcohol decreases with increasing molecular weight. How-

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[1] Scanlan, THIS JOURNAL, 57, 887 (1935).