conditions, since pure oxygen itself will not lead to oxidation. In other experiments, to be reported later, we have found that atomic oxygen acting on U_3O_8 gives rise to the same crystal modification of UO_3 (Phase I) as does nitrogen dioxide. As mentioned above, nitrogen dioxide is strongly adsorbed by the lower oxides. We would therefore like to suggest that the active reagent in the nitrogen dioxide oxidations is atomic oxygen, which originates from the adsorbed nitrogen dioxide when sufficient thermal energy is imparted to the molecule. In the absence of reliable adsorption and kinetic data, further speculation does not appear warranted. Assuming atomic oxygen mechanisms for reactions of the type discussed here, nitrogen dioxide reactions will be more favorable than molecular oxygen reactions by an amount corresponding to the difference in the heats of adsorption and heats of dissociation between nitrogen dioxide and molecular oxygen.

Acknowledgment.—We acknowledge with thanks the interest and cooperation of Dr. W. H. Zachariasen, Dr. R. C. L. Mooney, and members of their staff—Miss Ann Plettinger and Mr. Wallace Koehler, who were responsible for obtaining all of the X-ray data given here. Dr. Mooney in particular, contributed the interpretation of the neptunium oxide structure.

Summary

1. Nitrogen dioxide oxidation of U_3O_8 above $250°$ results in a brick-red anhydrous UO_3 with a crystal structure distinct from other known phases of UO_3.

2. Nitrogen dioxide oxidation of UO_2 results in products varying in composition from $UO_{2.2}$ to $UO_{2.9}$, depending on the temperature.

3. Treatment of Np(IV, V, VI) hydroxide precipitates (dried at $70°$) with nitrogen dioxide at $300-450°$ yields Np_3O_8, isomorphous with U_3O_8. Direct analysis of the product leads to the formula $NpO_{2.64 \pm 0.03}$.

4. Thermal decomposition curves of UO_3 and Np_3O_8 have been compared. The former shows a region of stability corresponding to the formula $UO_{2.91}$. The curve for Np_3O_8 shows no plateau but indicates a marked similarity in the thermal stabilities of UO_3 and Np_3O_8.

5. Attempts at the preparation of NpO_3 and higher oxides of plutonium, americium and protactinium were unsuccessful.

The Alkaline Hydrolysis of Ethyl Acetate from the Standpoint of Ion-Dipole Theory

BY JAMES EDWARD POTTS, JR.,[1] AND EDWARD S. AMIS[2]

We have been interested in the rates of reaction between ions and dipolar molecules. Among the reactions which have been studied have been the inversion of sucrose by hydrochloric acid,[3] the hydrolysis of ethylene acetal by perchloric acid,[3] and the hydroxide ion–diacetone alcohol reaction.[4] These reactions, the first two of which were of the positive ion–dipolar molecule type and the third of which was of the negative ion–dipolar molecular type, were discussed in relation to an equation derived[3] to explain ion–dipolar molecule reaction rates from a theoretical standpoint.

The alkaline hydrolysis of ethyl acetate was chosen for the purpose of further investigating the ion–dipolar molecule type of reaction. The velocity of the reaction is favorable for study and there are no complications, the strictly second order rate equation holding throughout.

Experimental

The ethyl acetate used in these experiments was a colorless sample purified as described by Weissberger and Proskauer.[5] The ethyl acetate was dried with anhydrous potassium carbonate and one gram of water added for each 250 g. of ester, after which it was distilled through a 36 inch column packed with $1/8$ inch single turn stainless steel helices and equipped with a total reflux partial take-off still head. Any alcohol remaining in the mixture passed off as a water–alcohol–ester azeotrope. The ethyl acetate which distilled at $77.1°$ under pressure of 760 mm. was stored in a pyrex erlenmeyer flask fitted with a ground glass stopper. One-gram samples of the material were analyzed, by adding twice the theoretical amount of standard sodium hydroxide solution, allowing the mixture to stand one hour at $70°$, and titrating the excess alkali with standard acid. The average of four analyses gave the ratio of moles of sodium hydroxide per mole of ethyl acetate reacting to be 1.0025.

The ethyl alcohol was purified by the method of Young as described by Weissberger and Proskauer.[5] One liter of 95% grain alcohol was refluxed for four hours with 300 g. of calcium oxide and distilled. A large middle fraction from this distillation was refluxed with calcium metal and distilled, yielding absolute alcohol. A middle fraction comprising about two-thirds of the material was retained for use.

Freshly boiled distilled water was used in the preparation of solutions containing water.

Carbonate-free sodium hydroxide stock solutions were prepared by dissolving chemically pure sodium hydroxide in water in a one to one weight ratio. The concentrated solution was allowed to stand in a covered container for twenty-four hours, after which the clear supernatant liquid

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(3) Amis and Jaffe, *J. Chemical Phys.*, **10**, 598 (1942).

(4) Amis, Jaffe and Overman, THIS JOURNAL, **66**, 1823 (1944).

(5) Weissberger and Proskauer, "Organic Solvents," Oxford University Press, London, 1935.

was decanted and filtered in order to remove sodium carbonate crystals. Stock solutions of 0.500 and 0.0500 N sodium hydroxide were prepared by diluting the one to one solution and were stored in paraffin-lined 10-liter bottles, equipped with soda-lime tubes to exclude carbon dioxide. The 0.0200 N sodium hydroxide solution used as a titrating agent was prepared in 2-liter batches at frequent intervals by diluting the 0.0500 N solution.

The 0.1000 N hydrochloric acid stock solutions were prepared from chemically pure concentrated acid and standardized against sodium carbonate. The 0.0200 N hydrochloric acid used in the titrations was prepared in 4-liter batches at frequent intervals by dilution of the stock solution.

Analytical weights and volumetric apparatus used in this investigation were calibrated using Bureau of Standards weights, and the thermometers were calibrated against Bureau of Standards thermometers. Since all of the experiments were made at temperatures lower than room temperature, it was necessary to circulate ice water through coils in the thermostatic water-bath. The temperature of the bath was controlled to $\pm0.01°$ with a Beckmann type mercury in glass thermo-regulator and a Sargent zero current relay.

The rate of the ester hydrolysis was studied in duplicate at 0, 9.8 and 19.1° in both pure water and in ethyl alcohol-water solutions. The dielectric constant data of Åkerlöf[6] were used to compute the proper weight percentages of the alcohol-water solutions to give dielectric constants of 80, 65 and 50 at the three temperatures.

Runs were also made at three temperatures at a constant dielectric constant of 65 and at ionic strengths μ of 0.0200, 0.0500, 0.1000, 0.2000, and 0.3000, sodium nitrate being used when required to regulate the ionic strength.

The kinetics of the reaction between ethyl acetate and sodium hydroxide was determined using the following procedure.

Three hundred milliliters of the desired solvent at the reaction temperature was pipetted into a 600-milliliter Kjeldahl flask. To this was added 100.00 ml. of 0.0500 N ethyl acetate at the same temperature. The flask was stoppered and allowed to reach temperature equilibrium in the thermostat, after which the reaction was initiated by pipetting 100.00 ml. of 0.1000 N sodium hydroxide at equilibrium temperature into the flask and shaking vigorously. Within the limits of volume change on mixing, the solution was initially 0.0100 N in ethyl acetate and 0.0200 N in sodium hydroxide.

After a few minutes a 50.00-milliter sample of the reaction mixture was withdrawn, drained into a measured excess of 0.0200 N hydrochloric acid at 0°, and titrated to the emerald green end-point of brom thymol blue with 0.0200 N sodium hydroxide using a 10-milliter machlette autoburet calibrated to the nearest 0.05 milliter.

Samples were removed and titrated at suitable intervals during the first 80% of the reaction, after which the flasks were kept at room temperature for twenty-four hours or until the reaction had gone to completion. The concentration of sodium hydroxide remaining in the flask after hydrolysis was completed was determined by replacing the flask in the thermostat, allowing it and the contents to come to the correct temperature and withdrawing and titrating two or three samples as described above. The average of these values was taken as the concentration of sodium hydroxide, C_∞, in the reaction mixture after the reaction is complete.

The reaction velocity constant, k', was calculated using the Reicher[7] equation where C_i is the concentration

$$k' = \frac{2.303}{tC_\infty} \log \frac{C_n(C_i - C_\infty)}{C_i(C_n - C_\infty)} \qquad (1)$$

of sodium hydroxide at time t_i, C_n is the concentration of sodium hydroxide at time t_n, C_∞ is as defined above, and t is the elapsed time $(t_n - t_i)$ in minutes.

The equation given above does not require extrapolation to zero time.

(6) Åkerlöf, THIS JOURNAL, **54**, 4125 (1932).

(7) Reicher, Ann., **228**, 257 (1885).

TABLE I

REPRESENTATIVE CALCULATIONS OF VELOCITY CONSTANTS FROM EXPERIMENTAL DATA

Pure water as solvent, temperature 0.00 °C., $D = 88.3$, NaOH $= 0.0200M$, EtOAc $= 0.0100M$

Time, min.	0.0200 M HCl, ml.	0.0200 M NaOH, ml.	C_n	k, liters/mole min.
0	60.0	11.50	0.01940	
15	50.0	7.35	.01706	1.10
30	50.0	11.20	.01552	1.09
45	50.0	13.95	.01442	1.09
60	50.0	15.95	.01362	1.08
75	50.0	17.55	.01298	1.09
	50.0	24.00	.01040	

Average $k = 1.09 \pm 0.01$

Data

In Table I are presented representative data taken on the reaction velocity constant. The table is illustrative of both the precision obtained and of the well-established fact that the reaction is strictly second order. The precision is given as the average deviation from the average.

The velocity constants at a dielectric constant of 65.0 and ionic strength ranging from 0.0200 to 0.3000, and at temperatures 0.00, 9.80 and 19.10° are recorded in Table II.

TABLE II

EXPERIMENTAL VALUES OF VELOCITY CONSTANTS AS A FUNCTION OF IONIC STRENGTH AND CORRESPONDING ENERGIES OF ACTIVATION AND FREQUENCY FACTORS

$D = 65$, NaOH $= 0.0200M$, EtOAc $= 0.0100M$. When necessary ionic strength was varied by addition of NaNO₃

μ γ	k' 0.00° 36.7% EtOH	k' 9.80° 31.5% EtOH	k' 19.10° 26.5% EtOH	ΔE	$B/2.3$
0.0200	0.519	1.41	3.02	14,625	11.42
.0500	.506	1.35	2.96	14,670	11.44
.1000	.495	1.29	2.92	14,750	11.49
.2000	.468	1.25	2.80	14,860	11.56
.3000	...	1.18	2.75	....	...

In this table are also given the energies of activation ΔE and the Arrhenius frequency factor B calculated from the equations

$$\Delta E = \frac{RT_1T_2}{T_2 - T_1} \ln \frac{k'_2}{k'_1} \qquad (2)$$

and

$$B = \frac{T_2 \ln k'_2 - T_1 \ln k'_1}{T_2 - T_1} \qquad (3)$$

respectively, where k'_1 and k'_2 are the reaction velocity constants at absolute temperatures T_1 and T_2, respectively, and R is the gas constant in calories per gram mole per degree. There is a slight dependence of both ΔE and B on ionic strength. The variations of these factors with ionic strength are reminiscent of like trends observed[8] and explained[9] theoretically in the case of ion–ion reactions.

(8) Amis and LaMer, THIS JOURNAL, **61**, 905 (1939).

(9) LaMer and Kamner, ibid., **57**, 2662 (1935).

The velocity constants obtained in various iso-dielectric media at an ionic strength of 0.0200 and at three different temperatures are given in Table III, together with the values of ΔE and B calculated from equations (2) and (3), respectively. The values of the energies of activation and of the Arrhenius frequency factor decrease with increasing dielectric constant of the media. The decrease of the energy of activation is predicted by the theory of coulombic energy of activation.[10] The magnitudes of the variations are larger than would be expected as will be discussed later.

The rate constants obtained in pure water and recorded in Table III are plotted in Fig. 1 together with data of other investigators in the same solvent. The data obtained in this investigation are
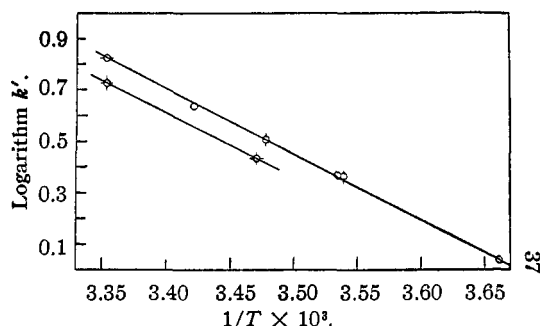

Fig. 1.—Logarithm k' versus $1/T$ for runs in pure water: O, Potts; ◊, Reicher; ⚬, Salmi and Korte; ⚬, Selivanova and Syrkin.

shown by this figure to be in agreement with the data for pure water solvent obtained by Reicher[11] and Salmi and Korte.[12] Two points by Selivanova and Syrkin[13] fall on a line of apparently nearly the same slope. The preponderance of data indicate that the values of k' obtained by Selivanova and Syrkin are too low. It will be observed in Table III that the values of k' in pure water (zero per cent. alcohol) show a slight reversal in trend with dielectric constant from the values of k' in the mixed ethyl alcohol–water solvents. In the mixed solvents the values of k' increase with increasing dielectric constant of the media, but the values of k' fall slightly in going from the mixed solvent of highest dielectric constant to pure water of still higher dielectric constant. The reversal of trend of the water points obtained in this investigation recalls a similar phenomenon in the acid inversion of sucrose in pure water as compared with dioxane–water media.[3,14] In the present investigation the variation of the data in the case of pure water as compared to ethyl alcohol–water is not so great as to eliminate the water data from consideration, and in comparison of the experi-

(10) Amis, THIS JOURNAL, **63**, 1606 (1941).

(11) Reicher, Ann., **228**, 257 (1885).

(12) Salmi and Korte, Ann. Acad. Sci. Fennicae, **A54**, No. 12, 13 pp. (1940).

(13) Selivanova and Syrkin, Compt. rend. (DOKLADY) de L'Academic des Sciences de L'URSS, **23**, No. 1, 45 (1939).

(14) Amis and Holmes, THIS JOURNAL, **63**, 2231 (1941).

mental data with theory the water runs are included.

To test the influence of ionic strength on the ethyl acetate hydroxide ion reaction, the equation[3]

$$\ln k' = \ln k'_{\kappa=0} +$$

$$\frac{\epsilon Z_B \cos \theta_0}{DkTr_0^2} (\mu_0{}^* - \mu^* e^{-\kappa r_0}(1 + \kappa r_0)) \quad (4)$$

was transformed by substituting in it the dimensionless variables

$$z = \kappa a = \kappa r_0 \quad (5)$$

and

$$W = (\ln k' - \ln k'_{\kappa=0})(2DkTr_0^2)/(\epsilon z_B \mu_0{}^* \cos \theta_0) \quad (6)$$

giving

$$W = \frac{z^2}{\left(1 + z + \frac{1}{2}z^2\right) + \frac{n^2}{2D}(1 + z)} \quad (7)$$

TABLE III

EXPERIMENTAL VALUES OF VELOCITY CONSTANTS AS A FUNCTION OF DIELECTRIC CONSTANT AND CORRESPONDING ENERGIES OF ACTIVATION AND ARRHENIUS FREQUENCY FACTORS

$\mu = 0.0200$, NaOH $= 0.0200M$, EtOAc $= 0.0100M$

	0.00° per cent.		9.80° per cent.		19.10° per cent.			
D	EtOH	k'	EtOH	k'	EtOH	k'	ΔE	$B/2.3$
88.3	0.0	1.09	...	...	..	..		
84.3	..		0.0	2.34	..	..		
80.7			...	...	0.0	4.34		
80.0	13.3	1.18	7.30	2.41	1.1	4.51	11,300	9.09
65.0	36.7	0.519	31.5	1.41	26.5	3.02	14,625	11.42
50.0	60.2	0.161	55.6	0.426	31.1	1.09	15,888	11.92
35.6	85.0	0.052	...	...	..	..	....	...

A theoretical curve, Fig. 2, of W versus z^2 was drawn, and the data (recorded in Table II and represented by the symbols) for the dependence of the velocity constant on ionic strength were fitted to the curve using the constants of Table IV. It can be observed from Fig. 2 that the

TABLE IV

CONSTANTS USED IN PLOTTING CURVES IN FIG. 2

$r_0 = 7.5$

Temp., °C., ±0.02	$\mu_0{}^* \times 10^{18}$	n^2	z^2 at ionic strength = 1	$k'_{\kappa=0}$
0.00	13.2	12.7	7.95	0.530
9.80	7.66	6.51	7.72	1.46
19.10	11.7	11.0	7.48	3.07

data fit the theoretical curve well. The radius r_0 of the critical complex, the enhanced moments $\mu_0{}^*$ and the squares of the internal refractive indices n^2 are comparable to the values of these constants found in former applications of this theory.[3,4] The radius of the intermediate complex was the same at all temperatures and resulted in reasonable and comparable values of $\mu_0{}^*$ and n^2. The values of $k'_{\kappa=0}$ were obtained by extrapolating k' as a function of μ at each temperature to $\mu = 0$. The enhanced moments were calculated using the equation

$$\mu_0{}^* = \frac{4.606DkTr^2 \, \Delta \log k'}{\epsilon z_B \cos \theta_0 \, \Delta W} \quad (8)$$

which is derivable from eq. 6. The n^2 values were obtained from the expression

$$\mu_0^* = \mu_0(n^2 + 2)D/(2D + n^2) \qquad (9)$$

using the value 1.8 Debye units for the moment μ_0 of ethyl acetate *in vacuo*.[15] In the actual calculation the value of n^2 in the denominator in eq. 9 was considered negligible with respect to $2D$. This will make the calculated values of n^2 somewhat low, but this manner of calculation was used to facilitate comparison of values obtained here with those made previously[3,4] using the same method. The more exact calculation at zero degrees taking an average value of the dielectric constant at 62.0 gives, for example, the value of 14.4 for n^2 compared with 13.2 by the approximate method.

For testing the effect of the dielectric constant of the media upon the rate of the alkaline hydrolysis of ethyl acetate, eq. 4 was again transformed by making the substitutions of the variables

$$\kappa^2 = \lambda^2/D \qquad (10)$$

$$\zeta = \lambda a = \lambda r_0 \qquad (11)$$

and

$$W' = \frac{(\ln k' - \ln k'_{\kappa=0})(2kT)}{\epsilon z_B \mu_0^* \lambda^2 \cos \theta_0} \qquad (12)$$
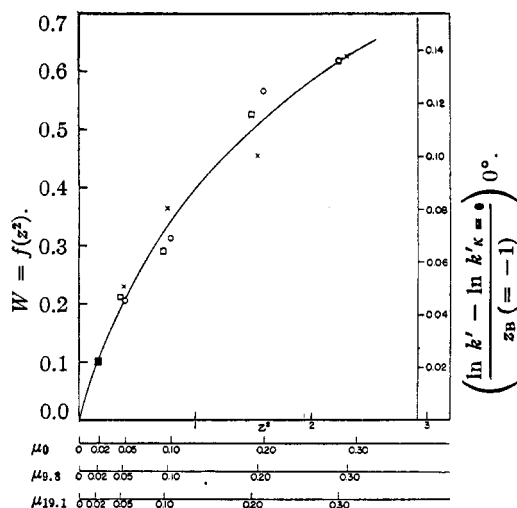

Fig. 2.—Agreement of μ data with theoretical curve, $W = f(z^2)$: O, $0°$; X, $9.8°$; ¶, $19.1°$.

$$\left(\frac{\ln k' - \ln k'_{\kappa=0}}{z_B (= -1)}\right)_{9.8°} = 1.546$$

$$\left(\frac{\ln k' - \ln k'_{\kappa=0}}{z_B (= -1)}\right)_{0°}$$

$$\left(\frac{\ln k' - \ln k'_{\kappa=0}}{z_B (= -1)}\right)_{19.1°} = 0.818$$

$$\left(\frac{\ln k' - \ln k'_{\kappa=0}}{z_B (= -1)}\right)_{0°}$$

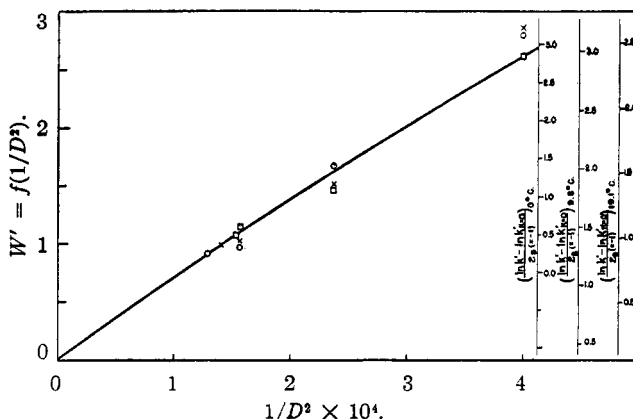(15) Sidgwick, Appendix, a table of dipole moments, *Trans. Faraday Soc.*, **30**, Appendix (1934).

Fig. 3.—Agreement of dielectric constant data with theoretical curve, $W = f(1/D^2)$: O, $0°$; X, $9.8°$; □, $19.1°$.

and obtaining

$$W' = \left(\frac{1}{D^2}\right)\left(\frac{1}{1 + \zeta/D^{1/2} + \zeta^2/2D}\right) \qquad (13)$$

A plot of W' versus $1/D^2$ was made, Fig. 3, and the dielectric dependent data recorded in Table III were fitted to the curve. The data are represented by the symbols in the figure. The line is from theory (Eq. 13). The fitting of the data to the theoretical curve however resulted in unreasonable values of at least two of the parameters, μ_0, n^2, or r_0. For example when r_0 was given the reasonable value of 7 Å., μ_0^* was 365×10^{-18}, 985×10^{-18}, and 863×10^{-18} and n^2 was 403, 1090, and 957 at $0.00°$, $9.80°$ and $19.10°$, respectively. These enormous values of μ_0^* and n^2 indicate an abnormally large dielectric constant effect upon the rate which is verified by the large variation of energies of activation of the reaction which dielectric constant as compared to the much smaller variation of these quantities with ionic strength. Compare Tables II and III.

According to the equation[16]

$$\Delta E = \frac{z_B \epsilon \mu_0}{D_1 D_2 r^2} \Delta D \qquad (15)$$

the coulombic energy of activation calculated from the data obtained in this investigation for the alkaline hydrolysis of ethyl acetate should be around 100 cal. The actual values are compared with calculated values in Table V. In this table are also recorded the enhanced moments necessary to make observed and calculated moments agree. In the case of the coulombic energy as in the case of the kinetic equation, it is evident that there is a large

TABLE V

ENHANCEMENT OF MOMENT OF ETHYL ACETATE AS GIVEN BY COULOMBIC ENERGY CONSIDERATIONS

Dielectric range	ΔE coulombic calculated	ΔE coulombic observed	Moment to make calcd. ΔE coulombic agree with obs. ΔE coulombic
65–80	51.3	3325	116.8
50–65	82.0	1255	27.5

(16) Amis, THIS JOURNAL, **63**, 1606 (1941).

enhancement of the moment with respect to the dielectric constant effect of the media.

The ethyl acetate–hydroxide ion reaction thus conforms with theory with respect to the effect of ionic strength upon the rate. With respect to the effect upon the rate of the dielectric constant of the media, theory merely reveals an abnormally large influence, the actual cause of which is obscure. With respect to the extrapolation to higher dielectric constant, it might be added that where reasonable enhanced moments have been found from dielectric effects, extrapolation to ionic strength equal to zero for ionic strength effects and to higher dielectric constants for dielectric constant effects have resulted in quite similar k' constants being obtained for the two extrapolations. In this instance the k' constants from the dielectric extrapolation were much larger (4 to 7 times) than from the ionic strength extrapolation. Thus the values of k' extrapolated from dielectric constant data were 3.80, 8.91 and 12.0 at 0.00, 9.80 and 20.0°, respectively, as compared to the $k_{x=0}$ values at the same three temperatures and listed in Table II.

Summary

1. The rate of the alkaline hydrolysis of ethyl acetate was studied both as a function of ionic strength and of the dielectric constant of the media at 0.00, 9.80 and 19.10°.
2. The ionic strength dependence of the rate was found to conform to the predictions of the ion–dipolar molecule rate theory proposed by Amis and Jaffe.
3. The dielectric constant influenced the rate of hydrolysis in the direction predicted by the ion–dipolar molecule theory, but the magnitude of the effect was very much greater than was expected from the standpoint of theory.

Cuprammonium–Glycoside Complexes. V. The Conformation of the Pyranose Ring in Some D-Hexose<1,5>β<1,6>Anhydrides

BY RICHARD E. REEVES

The hexosans of the levoglucosan type offer a particular opportunity for the study of pyranose ring conformations because only two of the eight theoretically possible Sachse strainless ring conformations satisfy the steric requirements of the hexosan rings. Thus, in order to make a definite assignment of ring conformation for substances of this type it is only necessary to choose between two possible ring forms.

Consideration of the properties of a large number of D-glucopyranosides[2] and D-galactopyranosides[3] has led to the observation that the existing data are in accord with assignment of a single one of the eight Sachse ring conformations to all of these simple pyranosides. This is the chair form designated C1, in which the ring oxygen atom and carbon atom 6 project on the same side of the plane of carbon atoms 1, 2, 4 and 5. However, it would be sterically impossible for a D-hexose anhydride of the levoglucosan type to possess this ring form.

The two pyranose conformations which, in the D-hexoses, are capable of forming hexosans of the <1,5>β<1,6> type are those designated 1C and 3B in an earlier communication.[2] These two ring

forms are shown diagrammatically in Fig. 1. There are apparently valid theoretical arguments favoring the chair form structures over the boat forms.[4] The hexosans offered a possibility of testing these arguments experimentally. The results indicate that for each of the ten D-hexosans examined it is indeed the chair form, 1C, which is adopted by the molecule in solution.

Discussion and Results

In a preceding article of this series[5] a theory has been presented which states that cuprammonium reacts with two hydroxyl groups to form a complex only when the two groups are located at or near a particular distance from each other. For hydroxyl groups on adjacent carbon atoms the complex-forming distance is realized when the groups are oriented at the true cis-position (0° angle) or at a 60° angle from each other. No complexes are formed at the 120 and 180° angles. When two hydroxyl groups on adjacent carbon atoms are oriented at the 60° angle it has been found to hold that when the angle, as previously defined,[5] is negative, cuprammonium produces a strongly levorotatory shift in optical rotation, and when the angle is positive, the shift is strongly dextrorotatory.

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) Reeves, THIS JOURNAL, **71**, 215 (1949).

(3) Reeves, ibid., **71**, 1737 (1949).

(4) Hassel and Ottar, Acta Chemica Scandinavica, **1**, 929 (1947).

(5) Reeves, THIS JOURNAL, **71**, 212 (1949).