[A JOINT CONTRIBUTION FROM THE MONSANTO CHEMICAL COMPANY AND THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Structure and Properties of the Condensed Phosphates. VI. Flow Birefringence

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RECEIVED JANUARY 19, 1952

Flow birefringence is measurable in solutions of $Na_2O-P_2O_5$ glasses and sodium or potassium Kurrol's salts, with the amount of birefringence at a given rate of shear or concentration being reduced by the addition of simple salts. As might be expected, it was found that the shorter the chain length of the polyphosphate anion the higher is the concentration at which birefringence is barely detectable. Theoretical calculations indicate that the birefringence is attributable directly to the chain anions, and it is believed that added salts cause these anions to lose their rigid configuration and thus to curl.

In the first paper[2] of this series a theory of the structure of phosphates in solution was developed. This theory indicated that all phosphates in aqueous solution can only consist of ring or chain polyanions in addition to the monomer (orthophosphate) anion. At present only two crystalline ring phosphates (the trimeta- and tetrametaphosphate) are known, and it is believed that the high molecular weight metaphosphates[3,4] as well as the vitreous phosphates[5] are composed entirely or to a large proportion, of chain polyanions. This being the case, one would expect that their solutions should[6] exhibit flow birefringence under the proper experimental conditions.

The instrument used in these studies can detect a birefringence, expressed in terms of $n_e - n_0$, of 8×10^{-8}. The limit of detectability for a given molecule or particle depends on its asymmetry, its principal refractive indices, the refractive index of the solvent, the maximum rate of shear used (which in this study was about 1.6×10^4 sec.$^{-1}$), and on its concentration. The experience of other investigators[7] indicates that, at a shear rate of the order of 10^4 sec.$^{-1}$ in solvents of viscosity of the order of a few hundredths of a poise, birefringence in low or moderately low concentrations of polymers cannot be detected if the major dimension of the particles is less than *ca.* 1,000 Å. This length corresponds to an extended P–O–P chain containing about 400 phosphorus atoms.

Experimental Details

The Salts.—The sodium thiocyanate and tetramethylammonium bromide were C.P. salts obtained from Mallinckrodt and Eastman Kodak, respectively. The sodium pyrophosphate, sodium tripolyphosphate and potassium tripolyphosphate were all Monsanto commercial products. Numerous careful studies have shown that these materials are chemically very pure and that nearly all of the phosphorus is present as the polymer indicated. Thus over 99% of the phosphorus in the pyro salt is present as the linear dimer. The small amounts of pyro- and metaphosphates in the tripolyphosphates were removed by recrystallization from water. The sodium phosphate glasses (including Graham's salt) were made and characterized in the same manner as previously described[5]; and the fibrous crystals of sodium Kurrol's salt were prepared according to the directions of Huber and Klumpner.[8]

Two preparations of potassium Kurrol's salt were studied: One was a sample from Monsanto regular commercial production and the other was prepared in the laboratory by heating KH_2PO_4 (Mallinckrodt C.P.) for 50 hr. at 550°. From the work of Malmgren and Lamm,[9] it is estimated that this latter material should have a molecular weight of *ca.* 10^6.

Most of the solutions studied were prepared by simple dissolution, although in some instances a short mixing time (1 min.) in a Waring Blendor was used to expedite the process. The solutions were clarified by centrifuging at 2×10^5 G. for 15 minutes.

It is believed that the sodium Kurrol's salt was considerably degraded during the process of dissolution, as the only way it could be dissolved was by milling a 1% aqueous suspension of its asbestos-like fibers for one hour in the Waring Blendor, which was kept in a cold room (*ca.* 4°) during that time to minimize thermally induced degradation. After sitting for 36 hr. this suspension turned to a gel which was centrifuged to remove undissolved particles. The sedimentation diagram from an ultracentrifuge study indicated that this solution was extremely polydisperse.

In spite of the fact that there was considerable degradation in the solution of sodium Kurrol's salt, it appears that there was no really low molecular weight material present, since orthophosphate ion could not be detected. The original sample of sodium Kurrol's salt was also believed to be free of other forms of $NaPO_3$ since the fibrous crystals were hand picked and, as an added precaution, carefully washed with water.

The average chain length of some of these preparations was determined by intrinsic viscosity measurements using the previously published relationship[10] between end-group titration and viscosity. These chain lengths are shown in Table I.

TABLE I

AVERAGE CHAIN LENGTHS

Phosphate	Method of characterization	Average number of P-atoms per polyphosphate chain
Potassium tripolyphosphate	X-Ray diffraction *p*H titration	3
Glass with Na_2O/P_2O_5 = 1.20	*p*H titration	10
Glass with Na_2O/P_2O_5 = 1.04	*p*H titration	50
Graham's salt (glass with Na_2O/P_2O_5 = 1) sample no. 1	*p*H titration Viscosity	147
Graham's salt (glass with Na_2O/P_2O_5 = 1) sample no. 2	*p*H titration Viscosity	218
Graham's salt (glass with Na_2O/P_2O_5 = 1) sample no. 3	*p*H titration Viscosity	255
Graham's salt (glass with Na_2O/P_2O_5 = 1) sample no. 4	*p*H titration Viscosity	275
Potassium Kurrol's salt (Monsanto commercial material)	Viscosity	475
Potassium Kurrol's salt	Viscosity	1430
Sodium Kurrol's salt (fibrous)	Viscosity	1000 (partially degraded)

The Instrument.—The flow birefringence was measured in an apparatus similar to the one described by Edsall, *et al.*[11] The critical dimensions of this apparatus were the

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[2] J. R. Van Wazer and K. A. Holst, THIS JOURNAL, **72**, 639 (1950).

[3] K. Plieth and C. Wurster, *Z. anorg. u. allgem. Chem.*, **267**, 49 (1951).

[4] H. Malmgren, *Acta Chem. Scand.*, **2**, 147 (1948); O. Lamm and H. Malmgren, *Z. anorg. u. allgem. Chem.*, **245**, 103 (1940).

[5] J. R. Van Wazer, THIS JOURNAL, **72**, 644 (1950).

[6] O. T. Quimby, *Chem. Revs.*, **40**, 172 (1947).

[7] J. T. Edsall, "Advances in Colloid Science," (Ed. E. O. Kraemer) Interscience Publishers, Inc., New York, N. Y., 1942, Vol. I, pp. 269–316.

[8] H. Huber and K. Klumpner, *Z. anorg. Chem.*, **251**, 213 (1943).

[9] O. Lamm and H. Malmgren, *ibid.*, **252**, 256 (1944).

[10] J. R. Van Wazer, THIS JOURNAL, **72**, 906 (1950).

[11] J. T. Edsall, A. Rich and M. Goldstein, *Rev. Sci. Instruments*, **23**, 695 (1952).

following: radius of inner cylinder = 1.242 cm., of outer cylinder = 1.270 cm., and height of inner cylinder = 3.64 cm. The outer cylinder rotated and both cylinders were machined from plastic (Bakelite). By having the outer cylinder rotate, turbulent flow does not begin until very high shearing rates are used.[12] For this instrument the critical gradient for the onset of turbulence in water was calculated to be 25,000 sec.$^{-1}$, a value which is nearly twice as large as the maximum gradient used.

All measurements were carried out on fresh solutions except where noted in the text.

Results

Salt-free Solutions.—Since the sodium Kurrol's salt was dissolved by purely mechanical means, it offers a good example of a solution of a very long chain polyphosphate free from added salts. As can be seen from Table II, this material exhibited very strong birefringence which was detectable at concentrations as low as 0.007%. The rotary diffusion constant, θ, of a prolate ellipsoid, having an axial ratio of ∞, which would show the same extinction angle at the given rate of shear was computed from the tables of Edsall, Scheraga and Gadd.[13]

It should be noted that the extinction angle, χ, is apparently independent of concentration, C, and diminishes only slightly as the rate of shear, σ, is increased. The lack of variation with concentration can probably be explained as the result of the competing effects of (1) the tendency of χ to increase on dilution as a result of lessening hydrodynamic and electrostatic interaction and (2) the tendency of χ to decrease with decreasing concentration as a result of a lowering in the shielding of the charges on the polymer, due to the spreading out of the counterion cloud and consequent extension of the chain. Additional evidence on this point is provided by the behavior of the amount of birefringence on dilution. In addition to the fact that χ is approaching its asymptotic value, the small change of χ with σ is probably also attributable in part to polydispersivity,[14] which lessens the usual drop in χ with increasing σ because more of the smaller asymmetric particles are lined up.

The amount of birefringence ($n_e - n_0$) divided by the concentration at a given shear either decreases or remains constant on dilution of solutions of large, non-charged molecules. In salt-free solutions of these polyelectrolytes, on the other hand (see Tables II and IV), this ratio increases as the concentration is reduced to those values where the measurement of $n_e - n_0$ is no longer regarded as being reliable ($n_e - n_0$ of the order of 5×10^{-7}). This may be interpreted as further evidence for the extension of the polyphosphate chains on dilution. Specifically, as the chain extends, the anisotropy of the molecule as a whole increases, with each chain element approaching parallelism to the chain axis. The ratio, $(n_e - n_0)/C$, appears to be a more sensitive criterion of shape changes than the behavior of χ. As can be seen in Table V, in the presence of added electrolyte $(n_e - n_0)/C$ either decreases or shows slight increases that are within experimental error.

TABLE II

FLOW BIREFRINGENCE DATA ON PURE AQUEOUS SOLUTIONS OF SOMEWHAT DEGRADED SODIUM KURROL'S SALT ($NaPO_3$)

Concn. (C) wt. %	Rate of shear (σ) sec.$^{-1}$	Extinction angle (χ) deg.	Double refraction ($n_e - n_0$) $\times 10^6$	$\frac{n_e - n_0}{C} \times 10^6$	Apparent rotary diffusion constant (θ) sec.$^{-1}$
0.90	3,100	6.8	+2.42	2.7	37
	6,580	5.5	3.45	3.8	55
	14,400	4.9	4.61	5.1	103
0.45	3,270	7.6	+1.75	3.9	46
	7,490	6.5	2.42	5.4	84
	14,800	6.2	2.84	6.3	156
0.24	3,390	8.4	+1.22	5.1	56
	7,390	7.9	1.51	6.3	111
	14,300	7.9	1.90	7.9	215
0.11	3,620	10.1	+0.95	8.6	91
	7,300	9.2	.97	8.8	146
	15,700	7.9	.98	8.9	236
0.056	3,650	9.2	+ .55	9.8	73
	8,060	8.7	.66	12	144
	13,900	9.4	.74	13	293
0.014	3,430	7.4	+ .41	29	47
	7,390	8.6	.45	32	129
	13,700	8.4	.53	38	226
0.007	12,700	Slight	Slight		

The variation of double refraction with rate of shear appears to be of the type[15] observed for rigid particles, and suggests that under the experimental conditions stretching of the particles by the velocity gradient is not playing a major role. As the double refraction, ($n_e - n_0$), is approaching a saturation value when χ is appreciably below 45°, it may be expected that this limiting value might be estimated by plotting $n_e - n_0$ against $1/\sigma$ and extrapolating to infinite shear. Extrapolation to infinite shear of birefringence data for a polydisperse system such as Graham's salt will naturally lead to an average value.[7,14] Thus the data of Table II are found to fit the empirical equation

$$(n_e - n_0)_{\sigma=\infty} = 0.6 \times 10^{-6} + (6.7 \times 10^{-6})\,C \quad (1)$$

The intercept term in this equation is to be connected with the apparent extension of the molecule on dilution.

In Table III the flow birefringence data for Graham's salts are presented. Because of the shorter chain length of this material, the lowest concentration at which birefringence can be detected is *ca.* 1% and the extinction angle is always very close to 45°. Measurements on these solutions are not very accurate for two reasons: First, at the higher concentrations measured, the solutions are quite viscous so the appreciable thermal gradients are set up at high shearing rates, the gradients in turn producing a blurring[16] of the image of the gap with a consequent loss in accuracy in χ. As the solution is diluted, this source of error disappears,

TABLE III

FLOW BIREFRINGENCE DATA ON PURE AQUEOUS SOLUTIONS OF GRAHAM'S SALTS ($NaPO_3$)

Average chain length (n)	Concn. (C) wt. %	Rate of shear (σ), sec.$^{-1}$	Extinction angle (χ), deg.	Double refraction ($n_e - n_0$) $\times 10^6$	$\frac{n_e - n_0}{C} \times 10^6$	Apparent rotary diffusion constant (θ), sec.$^{-1}$
275	30	4,240	43.6	+0.63	0.021	15,000
		6,440	44.1	1.03	.034	36,000
		12,200	(46.9)	1.16	.039	....
	15	5,770	44.6	+0.42	.028	7×10^4
		9,590	(46.1)	.48	.032	....
		16,200	(47.9)	.52	.035	....
	7.5	11,100	(45.8)	+ .16	.021	....
	3.8	14,500	44.8	+ .14	.037	3×10^4
	0.5	14,900	(45.2)	Slight	...	....
255	36.6	2,330	43.5	+0.86	0.023	7,300
		7,540	41.9	2.20	.060	11,500
	23.8	4,730	(42.7)	+0.20	.008	(9,700)
		8,250	43.9	.41	.017	35,000
		13,500	43.6	.58	.024	45,000
	12	8,800	(43.9)	+ .10	.008	(38,000)
		14,000	(44.3)	.17	.014	(9×10^4)
	1.9	15,080	45.1	Slight	...	....
218	38.7	3,640	42.8	+0.80	0.021	7,800
		5,920	43.2	1.31	.034	15,400
		9,300	44.0	1.65	.043	44,000
	25.0	5,060	(46.1)	+0.15	.006	....
		9,400	(45.4)	.28	.011	....
		15,600	45.2	.39	.016	....
	13	14,100	(46.5)	+ .12	.009	....
147	6.0	14,800	45.0	Slight	...	....

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(12) See, for example, H. G. Jerrard, *J. Applied Phys.*, **21**, 1007 (1950).

(13) H. A. Scheraga, J. T. Edsall and J. O. Gadd, Jr., *J. Chem. Phys.*, **19**, 1101 (1951).

(14) H. A. Scheraga, *ibid.*, **19**, 983 (1951).

(15) See P. Boeder, *Z. Physik*, **75**, 258 (1932), or A. Peterlin and H. A. Stuart, *ibid.*, **112**, 1, 129 (1939), as opposed to, say, W. Kuhn and H. Kuhn, *Helv. Chim. Acta*, **26**, 1394 (1943); *J. Colloid Sci.*, **3**, 11 (1948).

(16) Y. Bjornstahl, *Z. Physik*, **119**, 245 (1942).

TABLE IV

FLOW BIREFRINGENCE DATA ON SOLUTIONS OF COMMERCIAL POTASSIUM KURROL'S SALT (KPO_3) DILUTED WITH PURE WATER

Plasticizer and method of preparation of the most concentrated solution	Concn. (C), wt. %	Rate of shear (σ), sec.$^{-1}$	Extinction angle (χ), deg.	Double refraction ($n_e - n_0$) $\times 10^6$	$\frac{n_e - n_0}{C} \times 10^6$	Apparent rotary diffusion constant (θ), sec.$^{-1}$
NaCl used to ppt. plastic mass which was washed with water and then used to make a solution	0.9	2,760	19.2	+0.93	1.0	260
		6,200	16.4	1.67	1.9	420
		10,000	14.9	2.74	3.0	570
	0.45	2,760	18.6	+1.18	2.6	250
		6,200	16.4	1.66	3.7	420
		10,000	15.1^a	2.36	5.2	580
	0.9	2,670	20.0^a	+0.70^a	0.78	280
		5,250	16.9^a	1.25^a	1.4	300
		9,550	14.6^a	1.95^a	2.1	520
1 part Grahams salt to 10 parts potassium Kurrol's salt. Dissolved in water	1.0	10,000	15.2	+2.50	2.5	590
	0.5	2,760	21.3	+1.01	2.0	330
		6,200	18.5	1.19	2.4	580
		10,000	16.5	1.86	3.7	700
	0.17	2,760	20.0	+0.55	3.2	290
		6,200	18.2	.74	4.4	530
		10,000	16.2	.88	5.2	680
1 part $Na_5P_3O_{10}$ to 10 parts potassium Kurrol's salt. Dissolved in water	1.0	2,760	..	+ .49	0.49	..
		6,200	18.7	.69	.69	560
		10,000	16.6	.90	.90	700
	1.0	8,600	24.0^b	+ .53^b	.53	1300

[a] Partially hydrolyzed sample allowed to stand at room temperature (25°) for 24 hours. [b] Sample allowed to stand for 20 days at room temperature.

but the amount of birefringence also drops, so that χ again becomes hard to measure accurately. The values corresponding to badly blurred images of the gap are shown in parentheses in Table III. Because of the blurring, some of the parenthetical values of χ appear to be greater than 45°. There is no evidence, however, to indicate that this crossing of 45° is a real phenomenon.

Although it is impossible to obtain a solution of potassium Kurrol's salt free of simple salts without resorting to dialysis or some such complicated procedure, it was felt that measurements on this material, plasticized by a small amount of a salt of lower molecular weight followed by dilution with distilled water, could at least be extrapolated to interpretable values at infinite dilution. Flow birefringence data on such solutions are given in Table IV. Again it should be noted that the extinction angle is low, corresponding to long asymmetric particles.

The two short-chain $Na_2O-P_2O_5$ glasses were found to exhibit birefringence at high concentrations. Thus for a 40% solution of the $Na_2O-P_2O_5$ glass having a number average chain length, $\bar{n}$, of 50 phosphorus atoms per chain, χ = 34.2°, $(n_e - n_0) = +0.33 \times 10^{-6}$, and θ was computed to be 7,100 at a rate of shear of 17,000 sec.$^{-1}$. Also at the same concentration a similar glass for which $\bar{n} = 10$ gave $\chi = 23.8°$, $(n_e - n_0) = +0.14 \times 10^{-6}$, and a computed value of θ = 2,400 at σ = 15,500. At σ = 8,200 the birefringence was detectable but too small to measure. Neither glass gave detectable birefringence at a concentration of 20%.

Although the observation of birefringence in solutions of chains having fewer than 400 phosphorus atoms was not expected, it is to be noted that a distribution of chains ranging from *ca.* 4 to 30 phosphorus atoms ($\bar{n}$ = 10) showed birefringence. This may have several origins. For one the assumption of independent orientation is certainly not obeyed at such high concentrations (40%) even in the absence of complicating interactions of electrostatic origin. Certainly the mutual repulsion of the charges on the chains causes them to line up parallel to each other and hence to reinforce greatly the orientation due to flow. Also it is possible that the mechanism by which flow birefringence is produced in such systems may be related to the mechanism by which it is produced in pure liquids such as ethyl cinnamate rather than in high polymer solutions.[7]

Since sodium pyrophosphate and sodium tripolyphosphate are only moderately soluble, the necessary high concentrations for detectable birefringence could not be reached. However, potassium tripolyphosphate, which is soluble to the extent of *ca.* 180 g. per 100 g. water, also failed to exhibit birefringence at a concentration of 64% and a rate of shear of 16,400 sec.$^{-1}$.

The data given above demonstrate that the concentration at which birefringence is barely detectable appears to depend on the average chain length of the polyphosphate. If barely detectable birefringence is defined as a double refraction of *ca.* 0.1×10^{-6} at a rate of shear of 16,000 sec.$^{-1}$, Fig. 1 gives the concentrations below which birefringence cannot be observed on samples of various molecular weights.

As might be expected from their ring structures and solubilities, neither sodium trimeta- or tetrametaphosphates exhibited flow birefringence.

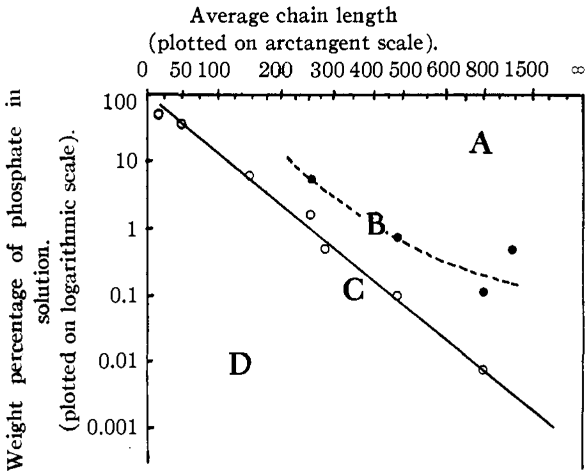


Fig. 1.—Logarithm of the concentration below which flow birefringence is not detectable plotted against the arctangent of the average polyphosphate chain length: A, region of observable birefringence; B, added salts; C, pure phosphate; D, no birefringence.

Solutions Containing Simple Salts.—The main effect encountered when salts of low molecular weight are added in large amounts to polyphosphate solutions is an appreciable diminution of the amount of flow birefringence. This effect is illustrated in Fig. 1.

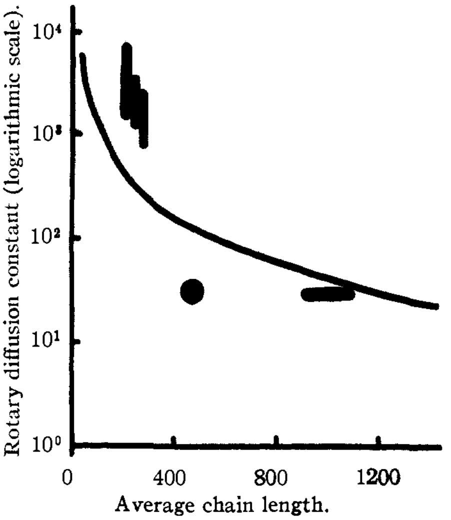


Fig. 2.—Rotary diffusion constant, θ, *vs.* average chain length, $\bar{n}$, with points calculated from experiment being compared to the theoretical curve from eq. (3) for polyphosphate molecule-ions.

In Table V it should be noted that again the amount of birefringence, $(n_e - n_0)$, is greatest for the materials which are believed to have the longest chains, as determined by end-group titration or intrinsic viscosity. These materials also exhibit the lowest extinction angles. Again it is seen that the extinction angle is relatively independent of concentration and rate of shear.

The double refraction at infinite rate of shear, estimated from extrapolating $(n_e - n_0)$ to $1/\sigma = 0$, appears to be roughly proportional to concentration as

$$\frac{(n_e - n_0)_{\sigma \to \infty}}{C} = k \qquad (2)$$

The k from the above equation is shown in Table V as a function of the polyphosphate chain length and the neutral salt added. As might be expected, k increases approximately proportionally to chain length when a given salt of low molecular weight is used. In tetramethylammonium bromide solutions the k increased faster with ascending $\bar{n}$ than in sodium thiocyanate solutions.

Discussion

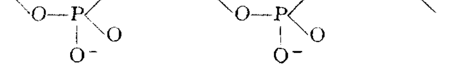
These flow birefringence studies offer independent evidence for the predominance of rod-type molecule-ions in solutions of the $Na_2O-P_2O_5$ glasses, including Graham's salt, and of both the sodium and potassium Kurrol's salts. The fact that the magnitude of the variables measured in the birefringence studies was found to be a function of average chain length (obtained directly from end-group titrations or from the correlation of end-group titrations with viscosity) indicates that the non-spherical units which are oriented in flow are probably the molecule-ions and not anisotropic agglomerates[17] which might be made up of approximately spherical ions. Qualitatively this is apparent in the data given in Fig. 1 which demonstrate the strong dependence of birefringence on ionic size. The existence of a salt effect, in which the birefringence is reduced by the addition of simple salts, confirms the conclusion that the molecule-ions themselves are oriented. This type of salt effect is universal for unassociated polyelectrolyte chains.

TABLE V

FLOW BIREFRINGENCE DATA ON POLYPHOSPHATES DISSOLVED IN SALT SOLUTIONS

Concn. (C), wt. %	Rate of shear (σ), sec.$^{-1}$	Extinction angle (χ), deg.	Double refraction $(n_e - n_0)$ $\times 10^6$	$\frac{n_e - n_0}{C}$ $\times 10^6$	Apparent rotary diffusion constant (θ), sec.$^{-1}$
Graham's salt, 255 P-atoms in av. chain, 0.2 M $Na_4P_2O_7$					
25	6,060	49.3	+0.39	0.015	..
	10,800	50.0	.82	.033	..
12.5	12,400	48.0	+ .23	.018	..
6.3	15,000	..	Slight	...	..
Commercial potassium Kurrol's salt, 475 P-atoms in av. chain, 0.4 M NaSCN; k from eq. 2 = 0.2 (wt. %)$^{-1}$					
5.0	4,460	25.9	+0.48	0.096	820
	8,110	26.1	.74	.148	1500
	15,400	23.0	.87	.174	2200
Commercial potassium Kurrol's salt, 475 P-atoms in av. chain, 10% $(CH_3)_4NBr$; k from eq. 2 = 0.4 (wt. %)$^{-1}$					
2.0	2,960	25.9	+0.09	0.045	540
	6,110	22.2	.24	.12	800
	14,000	18.3	.58	.29	1200
1.0	13,800	29.0	+ .16	.16	3400
Potassium Kurrol's salt, 1430 P-atoms in av. chain, 0.2 M $Na_4P_2O_7$; k from eq. 2 = 0.9 (wt. %)$^{-1}$					
10.0	7,540	8.5	+6.82	0.68	120
	11,970	9.0	7.29	.73	230
5.0	5,490	16.1	+1.41	.28	370
	13,600	11.8	2.72	.54	470
2.5	5,820	..	+0.89	.36	..
	13,800	15.0	1.19	.48	790
1.3	5,770	..	+0.42	.32	..
	13,690	..	0.61	.47	..
Potassium Kurrol's salt, 1430 P-atoms in av. chain, 10% $(CH_3)_4NBr$; k from eq. 2 = 1.8 (wt. %)$^{-1}$					
2.0	3,940	15.7	+0.47	0.24	250
	8,200	10.8	0.86	.42	240
	14,120	9.7	1.32	.66	320
1.0	6,340	13.4	+0.46	.46	290
	14,600	9.6	0.77	.77	320
0.5	14,170	..	Slight	..	..
Sodium Kurrol's salt, 1000 P-atoms in av. chain (broad size distribution) 0.4 M NaSCN; k from eq. 2 = 0.5 (wt. %)$^{-1}$					
1.0	7,630	11.8	+9.33	0.33	260
	15,400	14.3	0.42	0.42	800
Sodium Kurrol's salt, 1000 P-atoms in av. chain (broad size distribution) 10% $(CH_3)_4NBr$; k from eq. 2 = 1.1 (wt. %)$^{-1}$					
1.0	6,680	12.0	+0.43	0.43	240
	15,120	10.9	.76	0.76	440
0.50	13,700	9.6	+ .50	1.00	300
.25	13,600	9.2	+ .30	1.2	270
.13	15,400	..	Slight	..	..

In salt-free solutions it is reasonable to expect that the numerous negative charges on the polyphosphate chain would cause it to extend to its most elongated orientation as shown in the geometrical model



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[17] H. A. Scheraga and J. K. Backus, THIS JOURNAL, **73**, 5108 (1951); *J. Colloid Sci.*, **6**, 508 (1951).

According to this model the length in Å. of the stretched chain is 2.5 n and its diameter is *ca.* 3 Å. Thus the well-known equation[7] for the rotary diffusion constant of a prolate ellipsoid in terms of its major, a, and minor, b, semi-axes can be treated as shown below (assuming $\eta = 1.0$ centipoise)

$$\theta = \frac{3kT}{16\pi\eta a^3}\left[-1 + 2\ln\frac{2a}{b}\right] \approx \frac{1.32 \times 10^{11}}{\bar{n}^3}[-1 + 4.61 \log 1.64\bar{n}] \quad (3)$$

This relationship between θ and n is plotted in Fig. 2 where it is compared with the experimental points. These experimental points were obtained by empirically extrapolating the data of Tables II through IV to infinite rate of shear on plots of log θ *vs.* $1/\sigma$ and further extrapolating these values of $\theta_{\sigma = \infty}$ to zero concentration. Thus the points in Fig. 2 represent rough, average values of θ under conditions where the anions are not interfering with each other. The correspondence between the theoretical curve and the experimental points again indicates that the observed birefringence is of the right order of magnitude to be attributable to the fully stretched molecule-ions themselves. The lack of exact agreement between the curve and the points is attributable to inaccuracies and uncertainties in the physical model, the data and the extrapolation of θ to infinite rate of shear.

Since the rotary diffusion constant measured at a given concentration of a polyphosphate is considerably larger in the presence of added salts of low molecular weight than in pure solution, it can be inferred that the polyphosphate anion must assume a relaxed or curled position in the presence of the added salt. This inference is based on the assumption that the charges on an anion have no effect *per se* on birefringence measurements but only show up through the geometrical effects of their interaction.

Acknowledgment.—The kind interest and helpful comments of Professor Kurt G. Stern of Brooklyn Polytechnic are greatly appreciated.

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Decomposition of Nitrogen Pentoxide in the Presence of Nitric Oxide. III. Effect of Foreign Gases

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RECEIVED MAY 25, 1952

The decomposition of nitrogen pentoxide in the presence of nitric oxide has been studied in a 22-liter flask at 50.5° with added argon, nitrogen, carbon dioxide or sulfur hexafluoride. Reactant pressures were each about 0.08 mm. and foreign gas pressures varied from about 0.02 to 10 mm. By means of the general Lindemann mechanism for unimolecular reactions, it is shown that these data give the second-order activational rate constants for each reactant and for each foreign gas. The relative values of the limiting low-concentration rate constants are: A, 0.14; N_2, 0.23; NO, 0.30; SF_6, 0.32; CO_2, 0.40; N_2O_5, 1.00. From the data for each foreign gas an estimate is made of the mean-life with respect to decomposition of normally distributed activated reactant molecules; these estimates agree within experimental error. The application of this type of data to the problem of the form of the deactivational rate function is discussed.

Introduction

The initial rate of reaction of nitrogen pentoxide with nitric oxide is the rate of the elementary unimolecular reaction[1,2,3] $N_2O_5 \rightarrow NO_2 + NO_3$. With a slight excess of nitric oxide the initial rate continues unchanged for about three or four half-lives, and thus with this system it is easy to get a good measure of the rate constant of an elementary reaction. It is of great interest to study the effect of inert gases on the rates of unimolecular reactions, since this type of study gives the relative efficiency of various gases in activating the reactant molecule and some information about the form of the deactivational rate functions.

Experimental

The apparatus was the same as that described previously.[4] It consisted of a 22-liter Pyrex bulb in a stirred air thermostat. Two pipets of 0.001 volume of the flask and two pipets of 0.01 volume of the flask were connected by a three-way stopcock which permitted two gas samples to be passed simultaneously into the evacuated bulb. The reaction was followed by light absorption of nitrogen dioxide. An effort was made to improve the precision of results obtained from the apparatus. The light source was an AH-4 General Electric mercury arc stabilized by a Cenco constant voltage auxiliary. The IP 28 photo-multiplier tube was placed outside of the air thermostat to reduce dark current, since most runs were made at 50.5°. Many of the stopcocks were replaced by Corning high vacuum type and Greiner three-way high vacuum type. A McLeod gage was added, and the 22-liter bulb was evacuated to 10^{-4} mm. or lower before each run.

Nitrogen pentoxide and nitric oxide were prepared and purified as described before.[2] The foreign gases were Linde nitrogen, Stuart carbon dioxide and Matheson argon and sulfur hexafluoride. Nitrogen was passed directly from the tank through a liquid nitrogen trap into its storage bulb. Argon, carbon dioxide and sulfur hexafluoride were condensed by liquid nitrogen and fractionated into the storage bulb.

The carrying out of runs and the computation of rate constants were done as follows: The two large pipets were filled with a foreign gas to a known pressure. The two pipets were shut off from each other. One small pipet was filled to a known pressure with nitric oxide, and this was mixed with the foreign gas in one of its pipets. The second small pipet was filled with nitrogen pentoxide to a known pressure (as found by a null Bourdon gage), and this was mixed with the foreign gas in the other pipet. To start the reaction a three-way stopcock was turned so that it simultaneously passed into the 22-liter flask the nitric oxide plus foreign gas and the nitrogen pentoxide plus foreign gas. It has been established[4] that mixing was complete and temperature equilibrium was attained within three seconds. Before the run started the initial light intensity I_0 was obtained. Readings were made of light intensity every 3, 5 or 10 seconds depending on the rate of reaction. If the half-life was 6

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[1] J. H. Smith and F. Daniels, THIS JOURNAL, **69**, 1735 (1947).

[2] R. L. Mills and H. S. Johnston, *ibid.*, **73**, 938 (1951).

[3] H. S. Johnston, *ibid.*, **73**, 4542 (1951).

[4] H. S. Johnston and R. L. Perrine, *ibid.*, **73**, 4782 (1951).