

Fig. 8.—Plot of  $\mu$ -values against amount of heptane to cause cloud point.

solubility of polyvinyl chloride varies in these three solvents. Solutions of fraction 7 in the three solvents were titrated to the cloud point (visual examination) at 24 and 61° with *n*-heptane. The only correlation obtained was between  $\mu$ -values and the amount of heptane required for the cloud point. This is shown in Fig. 8, where  $\mu$  is plotted against the cc. of *n*-heptane necessary to bring a definite opalescence to 5 cc. of 0.5% solution of fraction 7. The intersection of the plot at zero amount of *n*-heptane occurs at a  $\mu$ -value of approximately 0.55. This is slightly greater than the critical value calculated from the theory<sup>4,5</sup> but corresponds closely to the value

determined from swelling experiments.<sup>18</sup> (This value of  $\mu$  separates solvents from non-solvents for small concentrations of polymer.) Such a correlation is another illustration that in dilute solution  $\mu$ -values are as practical as well as a thermodynamic measure of solvent ability.

**Acknowledgment.**—The authors wish to express their appreciation for the help of Dr. W. J. Badgley and Mrs. J. Bunker.

### Summary

1. The thermostating of a Fuoss-Mead type osmometer is described in detail together with the technique of operation at various temperatures.
2. Osmotic pressure measurements at several concentrations of polyvinyl chloride solutions in cyclohexanone, butanone-2 and dioxane over a 0–77° temperature range are reported.
3. The  $\mu$ -values and molecular weights are calculated from these measurements. The  $\mu$ -values may be represented as follows for fraction 7: cyclohexanone,  $\mu = 0.46 - 129/RT$ ; butanone,  $\mu = 0.47 - 36/RT$ ; dioxane,  $\mu = 0.16 + 203/RT$ .
4. The molecular weight depends on the solvent and the temperature (because of association).
5. To a good approximation the amount of *n*-heptane required to cause opalescence in polyvinyl chloride solutions is linearly dependent on the value of  $\mu$ .

(18) P. Doty and H. S. Zable, *J. Polymer Sci.*, **1**, 90 (1946).

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## The Solubility of Cellulose in Mixtures of Nitrogen Tetroxide with Organic Compounds

BY W. F. FOWLER, JR., C. C. UNRUH, P. A. MCGEE AND W. O. KENYON

Only a few types of solvents for cellulose are known including aqueous salt solutions, certain inorganic acids, inorganic bases at low temperatures, quaternary nitrogen bases, and complexes of copper with ammonia or organic amines. The existing knowledge of this field is summarized in recent texts,<sup>1,2</sup> which may be used as sources for references to experimental papers.

During a study of the oxidizing effect of oxides of nitrogen ( $\text{NO}_2$ ,  $\text{N}_2\text{O}_4$ ) on carbohydrates,<sup>3</sup> mixtures of the oxides with several classes of organic compounds were found to be solvents for cellulose.

(1) E. Heuser, "The Chemistry of Cellulose," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 136–164.

(2) H. M. Spurlin, "High Polymers," Vol. V in "Cellulose Derivatives," E. Ott, editor, Interscience Publishing Co., New York, N. Y., 1943.

(3) P. A. McGee, W. F. Fowler, Jr., E. W. Taylor, C. C. Unruh and W. O. Kenyon, *THIS JOURNAL*, **69**, 355–361 (1947). References to earlier papers of this series are given therein.

This paper is a preliminary qualitative description of such solvents.

### Experimental

**Materials.**—Nitrogen tetroxide of commercial grade purified as previously described.<sup>3</sup>

**Organic compounds** employed in the solvent mixtures were either Eastman Kodak Co. White Label Grade or were prepared by the usual synthetic methods and purified to meet the accepted values of boiling point or melting point. Liquid substances were tested for moisture with a small amount of anhydrous copper sulfate. If moisture was present, it was removed by shaking the liquid over anhydrous magnesium sulfate.

**Cotton linters** of good commercial quality and having a cuprammonium hydroxide viscosity of seven seconds were employed. They were ground to 20-mesh, then dried at 105° to constant weight.

**Substituted sulfonic esters** were synthesized by refluxing one mole of the sulfonyl chloride, 1.25 moles of the phenol and two moles of pyridine for eighteen hours. The reaction mixture was washed consecutively with water, dilute aqueous hydrochloric acid, water, dilute aqueous

sodium hydroxide and water. The residual oil was dissolved in 400 cc. of benzene and dried over anhydrous magnesium sulfate. Distillation of the benzene followed by vacuum distillation yielded the following compounds: phenyl benzenesulfonate, b. p. 191-192° (10 mm.); yield 54.6% of viscous, pale yellow oil which crystallized after several weeks.

*Anal.* Calcd. for  $C_{12}H_{10}SO_3$ : S, 13.67. Found: S, 13.83.

4-Chlorophenyl benzenesulfonate, b. p. 211-212° (10 mm.); yield 70.5% of liquid which finally crystallized.

*Anal.* Calcd. for  $C_{12}H_9SO_3Cl$ : Cl, 13.22; S, 11.91. Found: Cl, 13.06; S, 11.79.

**Methods.**—**Solubility tests** were conducted by first preparing in test tubes the desired solutions of  $N_2O_4$  and the organic compounds. Cotton linters were added and the mixtures were stirred. If solution did not occur, the tubes were closed and allowed to stand until it was evident that the composition was not a solvent.

**Regeneration** of dissolved cellulose was accomplished by pouring small quantities of solutions in 2-nitropropane- $N_2O_4$  (1:1) into a large volume of carbon tetrachloride. The regenerated cellulose was washed with carbon tetrachloride until the color of  $N_2O_4$  substantially disappeared, then with several changes of methanol, and finally with distilled water until the latter was neutral to brom thymol blue indicator. The perfectly white regenerated cellulose was air-dried at room temperature. The high viscosities of the dopes made it necessary to prepare several quantities which were precipitated separately and combined in the final sample.

Analyses of the cellulose recovered from solution to determine nitrogen and carboxyl contents employed techniques previously described.<sup>3</sup>

### Results and Discussion

A list of  $N_2O_4$ -organic compound mixtures which dissolve low-viscosity cotton linters is given in Table I. The heading "Wt. cellulose, g." indicates the amount of linters used in the test. The last column indicates the per cent. by weight of  $N_2O_4$  in the solvent mixture. In all cases 10 g. of the mixture was used for the amount of linters indicated.

The resulting solutions were quite clear, smooth and viscous with no "grain" or structure apparent on stirring. They flowed smoothly like viscous solutions of other macromolecular materials. The low-viscosity linters (seven sec.) and high solvent/cellulose ratios were used to facilitate the solubility tests. Higher-viscosity linters and lower solvent ratios produce very viscous solutions which are more difficult to stir and to determine when solution is complete. The percentages of  $N_2O_4$  used in these compositions are illustrative but are not limiting values. Rigorous purification of the acylated sugars and related esters was found necessary before they would act in combination with  $N_2O_4$  to produce cellulose solvents.

Solubility tests in selected  $N_2O_4$ /organic compound mixtures of various ratios are tabulated in Table II. The column "Solvent mixture units" indicates whether the per cent. of  $N_2O_4$  in the solvent mixture is on a weight basis (grams) or on a volume basis (cc.). If a weight basis was employed, 10 g. of the solvent was used for the indicated amount of cellulose, while on a volume basis, 10 cc. were used.

TABLE I  
 $N_2O_4$ -ORGANIC COMPOUND MIXTURES WHICH DISSOLVE CELLULOSE

Organic compound	Weight cellulose, g.	Weight % $N_2O_4$
2-Nitropropane	0.5	50
Nitrobenzene	.5	50
<i>o</i> -Dinitrobenzene	.5	"
<i>m</i> -Dinitrobenzene	.5	"
2,4-Dinitrochlorobenzene	.5	50
<i>o</i> -Nitrotoluene	.5	50
<i>p</i> -Nitrofluorobenzene	.5	50
$\alpha$ -Nitronaphthalene	.5	70
1-Chloro-1-nitropropane	.5	50
Dimethyl sulfone	.25	93
Di-(isobutyl) sulfone	.5	73
Phenyl isopropyl sulfone	.25	83
Dibenzyl sulfone	.50	80
Methyl acetate	.25	82
Ethyl acetate	.20	87
<i>n</i> -Amyl acetate	.25	83
Ethyl cyanoacetate	.25	80
Ethylene glycol diacetate	.13	88
2,3-Butanediol diacetate	.20	85
2-Ethylhexane-1,3-diol diacetate	.20	86
Triacetin	.20	83
Tributyryn	.20	85
Pentaerythritol tetraacetate	.20	85
D-Xylose $\beta$ -tetraacetate	.20	85
D-Glucose $\beta$ -pentaacetate	.13	88
D-Mannose $\beta$ -pentaacetate	.50	91
D-Galactose $\alpha$ -pentaacetate	.10	80
2,3,4,6-Tetraacetyl $\alpha$ -methyl glucoside	.13	87
<i>l</i> -Glucosan 2,3,4-triacetate	.15	88
Sorbitol hexaacetate	.15	88
Mannitol hexaacetate	.20	85
Cellobiose octaacetate	.13	88
Ethyl benzoate	.35	74
Phenyl acetate	.35	73
Phenyl benzoate	.20	85
Diphenyl phthalate	.20	85
Benzophenone	.20	85
4-Chlorobenzophenone	.20	81
2,4'-Dichlorobenzophenone	.20	81
4,4'-Dichlorobenzophenone	.20	81
Benzil	.20	81
$\beta$ -Naphthonitrile	.5	80
Succinonitrile	.5	90
<i>p</i> -Chlorobenzonitrile	.50	80
$\beta$ -Chloropropionitrile	.5	80

<sup>a</sup> Saturated solution in  $N_2O_4$ .

The vigorous oxidizing action of  $N_2O_4$  severely limits the classes of organic compounds which can be used with it in forming cellulose solvents. Ketones such as benzophenone (Table I) do not appear reactive at ordinary temperatures while alkyl or alkyl-aryl ketones often react at room temperatures. Ethers are very reactive with  $N_2O_4$ .

Esters appear unaffected by  $N_2O_4$  under the experimental conditions used and all of those tested (Table I) produced solvent combinations. Al-

TABLE II

Organic compound	Weight cellulose, g.	Solvent mixture units
Acetonitrile <sup>a</sup>	0.5	cc.
Benzonitrile	.5	cc.
$\alpha, \alpha, \beta$ -Trichloropropionitrile	.25	g.
Chloroacetonitrile	.25	<sup>b</sup>
Diphenyl sulfone <sup>c</sup>	.5	g.
Sulfonal <sup>c</sup>	.5	g.
Phenyl benzenesulfonate	.25	g.
4-Chlorophenyl benzenesulfonate	.25	g.
Phenyl 4-chlorobenzenesulfonate	.13	g.
4-Chlorophenyl 4-toluenesulfonate	.13	g.
Diethyl sulfate	.5	cc.
Di- <i>n</i> -butyl sulfate	.13	cc.
Diphenyl sulfate	.13	cc.
1-Nitropropane	.5	cc.
2-Nitropropane	.5	cc.
2-Chloro-2-nitropropane	.5	cc.

Organic compound	N <sub>2</sub> O <sub>4</sub> , % <sup>d</sup>										
	10	20	25	30	40	50	60	70	75	80	90
Acetonitrile	s	s		s	sw	sw	sw	s-		s	s
Benzonitrile	sw	s-		s	s	s	s	s		s	p.s
$\alpha, \alpha, \beta$ -Trichloropropionitrile	i	s.sw		sw	s	s	s-	p.s.		i	i
Chloroacetonitrile			sw			p.s			s		
Diphenyl sulfone						s <sup>e</sup>	s	s			s
Sulfonal						s <sup>e</sup>	s	s		s	s
Phenyl benzenesulfonate	i	i		i	p.s	s	s	s		s	sw
4-Chlorophenyl benzenesulfonate	i	i		i	s.sw	s	s	p.s		p.s	i
Phenyl 4-chlorobenzenesulfonate						s <sup>e</sup>	s	s		s	s.sw
4-Chlorophenyl 4-toluenesulfonate					sw	p.s	s	s		s	s.sw
Diethyl sulfate	i	p.s		s	s	s	s	s		s	p.s
Di- <i>n</i> -butyl sulfate	i	s	s-			sw			i		
Diphenyl sulfate		s.sw				s.sw				s.sw	
1-Nitropropane	s	s		s	s	s	s	s		p.s	i
2-Nitropropane	s.sw	sw		s-	s	s	s	s		i	i
2-Chloro-2-nitropropane	i	i		i	p.s	s	p.s	p.s		p.s	i

<sup>a</sup> Becomes insoluble at about 5% N<sub>2</sub>O<sub>4</sub>. <sup>b</sup> Grams of nitrile and cc. of N<sub>2</sub>O<sub>4</sub>; thus 75% = 2.5 g. nitrile with 7.5 cc. of N<sub>2</sub>O<sub>4</sub>. <sup>c</sup> Cellulose incompletely soluble at 93% N<sub>2</sub>O<sub>4</sub>; insoluble at 95%. <sup>d</sup> Organic compound incompletely soluble in N<sub>2</sub>O<sub>4</sub>. i = insoluble, s.sw = slightly swollen, sw = highly swollen, s = soluble, s- = almost completely soluble—may contain haze, p.s. = partly soluble with swollen residue. <sup>e</sup> Organic compound incompletely soluble in N<sub>2</sub>O<sub>4</sub>.

though the gamut of alkyl groups and acyl radicals was not explored, esters of both the aliphatic and aromatic acids were successful. Esters of several monohydric alcohols, phenols, and polyhydric alcohols including carbohydrates and related substances, were satisfactory. It would then appear that carboxylic esters generally would serve.

Organic compounds containing sulfur in a higher valence state, as in sulfones, sulfates and sulfonic esters, form solvent combinations. Several phenyl esters of aromatic sulfonic acids formed solvents within a limited range of about 40 to 80% of N<sub>2</sub>O<sub>4</sub> (Table II).

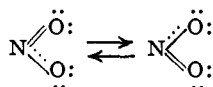
The esters of sulfuric acid showed a marked relationship between structure and solvent power. While diethyl sulfate formed solvent mixtures with N<sub>2</sub>O<sub>4</sub> in ratios of 30 to 80%, di-*n*-butyl sulfate formed a solvent only at 20 to 30%. Diphenyl sulfate did not form a solvent combination. In contrast, the sulfones including diphenyl sulfone were active in producing solvent compositions.

Nitriles of various types are effective in producing solvents. Benzonitrile was outstanding for the wide ratio in which it was effective.

The aromatic nitro compounds are generally effective when mixed with an equal weight of N<sub>2</sub>O<sub>4</sub>. 1-Nitropropane and 2-nitropropane are effective over the wide range of 10 to 70% of N<sub>2</sub>O<sub>4</sub>. In comparison, 1-chloro-1-nitropropane and 2-chloro-2-nitropropane produced solvents only in the very critical concentration ranges of about 50% of N<sub>2</sub>O<sub>4</sub> by weight and by volume, respectively. Extensive tests with 1,1-dichloro-1-nitropropane and 1,1-dichloro-1-nitrooctane produced no solvent combinations at any N<sub>2</sub>O<sub>4</sub> concentration.

Cellulose molecules are held together intermolecularly by hydrogen-bonding involving hydroxyl groups. To dissolve the cellulose, these bonds must be broken and the hydroxyl groups solvated. This mechanism, as applied to the solution of cellulose derivatives, has been recently summarized.<sup>2</sup> From the data of the present paper, we cannot de-

termine whether the oxides of nitrogen or the organic compounds solvate the hydroxyl groups. It is significant that a water-soluble cellulose acetate<sup>4</sup> swells greatly in liquid  $N_2O_4$  without added organic compound. Inasmuch as  $N_2O_4$  forms a solvent combination for cellulose in the presence of such a wide variety of organic liquids, it seems quite possible that  $NO_2$  solvates the cellulose molecule through hydrogen-bridging with the hydroxyl groups. Throughout this paper the oxides of nitrogen employed have, for simplicity, been referred to as  $N_2O_4$ , but actually an equilibrium mixture of  $N_2O_4$  and  $NO_2$  is meant. At the boiling point (294.25°K. at atmospheric pressure),  $N_2O_4$  is dissociated according to the equilibrium,  $N_2O_4 \rightleftharpoons 2NO_2$ , to the extent of 16.1 mole per cent.<sup>5</sup> The exact degree of dissociation might well be different in the presence of the various organic compounds used in this research. Nitrogen dioxide has a peculiar electronic structure, containing an odd number of valency electrons.<sup>6</sup> While this undoubtedly accounts for its ready dimerization and might render it readily additive to the cellulose molecule, the  $NO_2$  molecule is stabilized to a degree by resonance<sup>7</sup> between two equivalent three-electron bonded structures



There is some uncertainty concerning the electronic structure of the dimer molecule. Affinity of monomeric  $NO_2$  for cellulose, however, as an explanation of the solution mechanism has certain disadvantages. Many of the solvent combinations require large proportions of  $N_2O_4$ , which may indicate that the organic compound solvates the cellulose and this solvated molecule then dissolves. Acetonitrile (Table II) forms a solvent combination at two concentration ranges. Its effectiveness with small amounts of  $N_2O_4$  may indicate that the cellulose solvated by  $NO_2$  dissolves in excess acetonitrile, while at the other end of the scale, cellulose solvated by acetonitrile dissolves in the excess  $N_2O_4$ .

An electronegative group in the organic molecule appears to be a prerequisite to forming solvent mixtures for two possible reasons. Substances containing one or more electropositive groups react in a highly exothermic manner with  $N_2O_4$ ; furthermore, addition compounds between the organic substance and the  $N_2O_4$  may be of fundamental importance. The results obtained with the use of the various nitroparaffins and halogenated nitroparaffins show that such substances decrease in solvating power in combination with  $N_2O_4$  as the carbon atom, to which the highly electronega-

tive nitro group is attached, is further substituted by more electronegative groups, such as one or two chlorine atoms. This produces a net decrease in the effective electronegativity of the molecule, since the vector sum of the electronegativities of all the groups attached to a carbon atom determines the moment imparted to the molecule by the group.

In considering the solvating group or linkage in esters and ketones, it may be of some significance that Dry Ice swells 7-second cotton linters in liquid  $N_2O_4$  at low temperatures, thus pointing to the carbonyl group as the essential one in the aforementioned compounds.

Hydrolyzed cellulose acetate (about 16% acetyl content) and cellulose triacetate were soluble in compositions containing  $N_2O_4$  and certain aliphatic nitro compounds, though they were not soluble in either liquid alone. Such behavior is analogous to the solubility of acetone-soluble cellulose acetate in ethylene chloride containing a small amount of a lower aliphatic alcohol though it will not dissolve in either compound singly.<sup>2,8</sup> It is well known that cellulose acetate also dissolves in acetic acid- $N_2O_4$  compositions.

The cellulose may be recovered from solutions in  $N_2O_4$  and a volatile organic compound by flowing the dope onto a surface and allowing evaporation. Clear coherent cellulose sheetings result. The cellulose may also be precipitated by pouring the dope into a non-solvent, such as carbon tetrachloride, in which case it may be obtained in a variety of forms, including threads.

Analyses of low-viscosity cellulose regenerated from solution in 2-nitropropane- $N_2O_4$  (1:1), corrected to dry basis, were as follows: 5.58% moisture; 0.40% carboxyl by calcium acetate; 1.95% carboxyl by uronic acid; 0.54% nitrogen; 0.14 cps. cuprammonium viscosity of 0.35% solution of regenerated cellulose; 1.80 cps. cuprammonium viscosity of 0.35% solution of original linters. Only a small amount of oxidation to yield carboxyl groups occurred during the course of solution and regeneration. Nitration was not profound. Interpretation of the viscosity measurements is complicated by degradation of the regenerated cellulose, due presumably to the high pH of the cuprammonium hydroxide solution. Samples of the regenerated cellulose and the original linters were nitrated and acylated. Esters of the former were insoluble in organic solvents, including those which dissolved the latter. This indicates intermolecular links resulting from solution and regeneration or from esterification.

It may be that cellulose does not dissolve without change. The small amounts of oxidation or nitration indicated may be necessary for solution. The solutions usually set to a gel on standing. It is possible that nitration or oxidation products of the various organic compounds are the effective

(4) Of the type described by C. R. Fordyce, U. S. Patent 2,129,062 (September 6, 1938).

(5) W. F. Gianque and J. D. Kemp, *J. Phys. Chem.*, **6**, 40 (1938).

(6) N. V. Sidgwick, "The Electronic Theory of Valency," Clarendon Press, Oxford, 1927, pp. 211-279.

(7) L. Pauling, "The Nature of the Chemical Bond," 2nd edition, Cornell University Press, Ithaca, New York, 1940, p. 270.

(8) Lindsay, U. S. Patent 1,027,616 (1911); for discussion of quantitative experiments, see S. E. Sheppard and S. S. Sweet, *J. Phys. Chem.*, **36**, 819 (1932).

agents in forming solvent combinations with the  $N_2O_4$ . cursory examination of such combinations gave no indication of such reactions.

In testing the solubility of cellulose in compositions containing  $N_2O_4$ , it is necessary scrupulously to avoid the presence of water, as indicated in the experimental portion. The seven-second cotton linters will dissolve readily in a mixture of 15 parts by volume of pure  $N_2O_4$ , to which is added one part of water. It appears that  $N_2O_3$  may be important in determining this solubility for, in comparison,  $N_2O_4$  and pure nitric acid in the ratios comparable to those given do not form a solvent mixture. Aryl sulfonates are seen to be solvents with  $N_2O_4$  for cellulose, but it was impossible to ascertain whether the free aryl sulfonic acids are effective, inasmuch as these bodies are hydrated and strongly hygroscopic.

The several properties which are necessary for producing new solvent combinations for cellulose by the scheme followed in this research may be listed as: (1) a substance having a three-electron bond plus (2) a substance having the following properties: (a) at least one electronegative group stabilized by resonance; (b) either no reactivity with or very slow reactivity with substance (1); (c) miscible with or soluble in the substance (1);

(3) the combination of (1) plus (2) in the proper ratios either does not react with cellulose or reacts at a very slow rate which does not interfere with its utility.

### Summary

1. A novel type of cellulose solvent or peptizing agent is described which involves the use of a mixture of liquid nitrogen tetroxide and a second (organic) substance miscible with or soluble in this oxide of nitrogen.

2. The second substance must contain an electronegative group in the molecule and exhibit very slow reactivity or none with nitrogen tetroxide as well as a useful range of miscibility or solubility with the latter.

3. Such addends to nitrogen tetroxide include nitroparaffins, certain aromatic nitro compounds, sulfones, nitriles, aryl sulfonates, diaryl ketones, and aromatic, aliphatic and aromatic-aliphatic esters, as well as many others.

4. The effect of such solvent mixtures on the properties of cellulose regenerated therefrom is described; oxidation is extremely slow.

5. Several theories are discussed which might be used to explain these phenomena.

ROCHESTER 4, N. Y.

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[CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, AND ILLINOIS STATE WATER SURVEY]

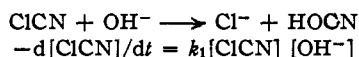
## Hydrolysis and Chlorinolysis of Cyanogen Chloride<sup>1</sup>

BY CHARLES C. PRICE,<sup>2</sup> T. E. LARSON,<sup>3</sup> KARL M. BECK, F. C. HARRINGTON,<sup>4</sup> L. C. SMITH AND ILYA STEPHANOFF

This investigation was undertaken to obtain information concerning the reactivity of dilute aqueous solutions of cyanogen chloride. It was of interest to determine not only the rate of hydrolysis but the reaction, if any, with chlorine or hypochlorite.

### Experimental

**Hydrolysis.**—It has long been known that alkali reacts readily with cyanogen chloride.<sup>5</sup> Alkaline cleavage is sufficiently rapid and complete to be useful analytically by titrating the chloride ion so liberated.



By measurement of the rate of this hydrolysis in alkali and bicarbonate-buffered solutions, the value for the rate constant,  $k_1$ , for the second-order

(1) The work reported here was done under a contract, recommended by the National Defense Research Committee, between the Office of Scientific Research and Development and the University of Illinois.

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(4) The services of F. C. Harrington were available through the courtesy of Wallace and Tiernan, Inc., Newark, New Jersey.

(5) Sartori, "The War Gases," D. Van Nostrand Co., New York, N. Y., 1939, p. 140.

reaction between cyanogen chloride and hydroxyl ion has now been estimated to be  $6 \times 10^2$  liters mole<sup>-1</sup> min.<sup>-1</sup> at 25°.

In phosphate buffer, the rate of disappearance of cyanogen chloride was considerably greater than expected for the observed hydroxyl ion concentration. It thus seems that phosphate has a specific accelerating action. The increase in rate could be satisfactorily accounted for by a second-order reaction of phosphate with cyanogen chloride with a rate constant,  $k_2$ , of  $3 \times 10^{-2}$  liters mole<sup>-1</sup> min.<sup>-1</sup>. The equation is written for monoacid phosphate ion although it is recognized that at the pH used (7.5) there will be an equilibrium distribution between various phosphate ions, any one of which *might* be the reactive species. The value given for  $k_2$  thus includes a factor expressing the fraction of total phosphate ions present in the form of the reactive species.<sup>5a</sup>

(5a) One might speculate that a hydrated phosphate ion might form an ion-dipole association complex with cyanogen chloride of the following configuration. Because of the geometry of the phosphate anion, such a complex could decompose to the products outlined above by the simple shift of electrons. The original ion-dipole bonds are indicated by dotted lines, the postulated electron shifts by dashed arrows.

