The Molecular Structures of Sulfuryl Fluoride and Thiophosphoryl Fluoride

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The relations between bond length and bond character in molecules containing bonds of the type sometimes called semipolar are not well understood. Among the compounds of phosphorus and sulfur there are a great number of such molecules, some of which have been investigated recently.[2,3,4] In this paper we give the results of an electron diffraction investigation of the structures of two such molecules containing fluorine atoms as well as semipolar double bonds.

Experimental.—The electron diffraction apparatus used in this investigation has been described by Brockway.[5] The camera distance was 10.84 cm., and the wave length of the electrons, determined in the usual fashion,[5] was 0.0611 Å.

Fifty cc. (S. T. P.) of pure thiophosphoryl fluoride was given to us by Professor H. S. Booth and Miss M. C. Cassidy of Western Reserve University, who have described the preparation and purification of the substance.[6] The sample was transferred to a bulb of about 150 cc. capacity which could be attached to the apparatus by means of a ground joint.

The preparation and purity of the sulfuryl fluoride used will be described in a separate paper on the Raman spectrum of this compound.[7] The pressure of the gas in the sample bulb was approximately 200 mm.

Interpretation.—Both the radial distribution method[8] and the correlation method[9] were used in interpreting the electron diffraction photographs. The modified radial distribution formula

$$D(l) = \sum_n C_n \frac{\sin s_n l}{s_n l} \quad C_u = f(I_n, s_n) \tag{1}$$

has been discussed by Schomaker.[10]

(1) National Research Fellow.
(2) L. O. Brockway and J. Y. Beach, THIS JOURNAL, **60**, 1836 (1938).
(3) K. J. Palmer, ibid., **60**, 2360 (1938).
(4) J. Y. Beach and D. P. Stevenson, J. Chem. Phys., **6**, 75 (1938).
(5) L. O. Brockway, Rev. Mod. Phys., **8**, 231 (1936).
(6) H. S. Booth and M. C. Cassidy, Boston, A. C. S. meeting, September, 1939.
(7) Horace Russell, Jr., and D. M. Yost, to be published.
(8) L. Pauling and L. O. Brockway, THIS JOURNAL, **57**, 2684 (1935).
(9) L. Pauling and L. O. Brockway, J. Chem. Phys., **2**, 867 (1934).
(10) V. Schomaker, Baltimore, A. C. S. meeting, April, 1939.

It has been remarked in the literature[9,11] that the coefficients $Z_i Z_j$ in the simplified theoretical scattering formula ordinarily used

$$I(s) = \sum\sum Z_i Z_j \frac{\sin l_{ij}s}{l_{ij}s} \tag{2}$$

are not completely satisfactory when the atoms i and j are members of different rows of the periodic system, and that the more exact expression

$$I(s) = \sum\sum (Z_i - f_i)(Z_j - f_j) \frac{\sin l_{ij}s}{l_{ij}s} \tag{3}$$

should be used. Since the corresponding coefficients in (2) and (3) differ by as much as 30% when $4 \leqslant s \leqslant 10$ for sulfuryl fluoride and thiophosphoryl fluoride, it was thought that it might be necessary to use (3) rather than (2) in the application of the correlation method to the interpretation of the photographs of these molecules. However, curves calculated according to (2) and (3) were found to be indistinguishable qualitatively and to have differences in the position of their maxima and minima of about 1% within the range of s indicated above. Since for $s \leqslant 12$ the coefficients of (2) and (3) are the same within 2%, it is thus satisfactory to use (2) rather than (3) in interpreting the photographs of sulfuryl fluoride and thiophosphoryl fluoride when $s > 12$. When $s < 12$ the photographs were compared with curves calculated according to (3).

Inasmuch as the two molecules under consideration are rather rigid, it was thought unnecessary to include a temperature factor[5] in the coefficients of the scattering formulas.

Sulfuryl Fluoride.—The photographs of this molecule show seven measurable maxima, six measurable minima, and two shelf-like features. The first shelf, designated a, is a shoulder on the inner side of the first maximum. The second shelf, feature b, is on the outside of the third maximum. The intensities of the maxima decrease uniformly from the first through the seventh. The only irregularity in the decreasing depth of the minima is that the fifth minimum is shallower than either

(11) M. H. Pirenne, J. Chem. Phys., **7**, 144 (1939).

the fourth or sixth minimum. The visually estimated relative intensities and the measured values of $s\left(s_0 = \frac{4\pi}{\lambda}\sin\frac{\vartheta}{2}\right)$ of the maxima and minima are given in columns 3 and 5 of Table I.

TABLE I

Max.	Min.	I_0	C_n	s_0	s^a	s^a/s_0	s^b	s^b/s_0
a		5	2	3.43	...	....	...	....
1		10	6	5.81	5.54	$(0.954)^c$	5.57	$(0.959)^c$
	2	−9	−7	7.22	7.24	1.003	7.22	1.000
2		8	8	8.80	8.92	1.014	8.92	1.014
b		4	5	11.21	...	....	...	....
	3	−6	−8	12.26	12.09	0.986	12.03	0.981
3		6	8	13.92	13.89	0.998	13.72	0.986
	4	−4	−6	15.41	15.48	1.005	15.42	1.001
4		4	6	16.77	16.94	1.010	16.91	1.008
	5	·−2	−3	17.82	18.12	1.017	18.00	1.010
5		3	5	19.10	19.10	1.000	19.01	0.995
	6	−3	−6	20.51	20.49	0.999	20.50	1.000
6		2	4	22.09	21.89	.991	21.83	0.988
	7	−1	−2	23.25	23.22	.999	23.21	.998
7		1	2	25.02	24.55	$(.981)^c$	24.49	$(.979)^c$

Average of 11 features   1.002 ± 0.007   0.998 ± 0.008

[a] From curve for model with S − F/S − O = 1.56/1.43. F − O/S − O = 2.36/1.43.   [b] From curve for model with S − F/S − O = 1.56/1.43, F − O/S − O = 2.38/1.43.   [c] Omitted from average.

The radial distribution function (1), calculated with the coefficients C_n of column 4, Table I, is shown in Fig. 1, curve B. The first maximum at 1.48 Å. is an unresolved average of the sulfur–oxygen and the sulfur–fluorine distances. If one assumes the sulfur–oxygen distance to be 1.43 Å., the distance found in sulfuryl chloride,[4] one may estimate the sulfur–fluorine distance to be 1.52 Å. Since the term involving the fluorine–oxygen distance is four times as important in the scattering formula as the terms involving the fluorine–fluorine and oxygen–oxygen distances, the second peak at 2.37 Å. probably corresponds closely to the fluorine–oxygen distance.

If one assumes, as has been found to be the case for sulfuryl chloride,[4] that the sulfuryl fluoride molecule is a bisphenoid with symmetry C_{2v}, there are three parameters which determine the form of the intensity curves. These may be conveniently taken as ρ_1, the ratio of the sulfur–fluorine to sulfur–oxygen distance, ρ_2, the ratio of the fluorine–oxygen to sulfur–oxygen distance, and β, the fluorine–sulfur–fluorine angle.

The radial distribution function indicates that the value of ρ_1 is in the vicinity of 1.52/1.43 and the value of ρ_2 is near 2.37/1.43. Eighteen curves were calculated,[2] for models with the parameters ρ_1 and ρ_2 in the ranges 1.48/1.43 ≤ ρ_1 ≤ 1.60/1.43 and 2.32/1.43 ≤ ρ_2 ≤ 2.44/1.43.
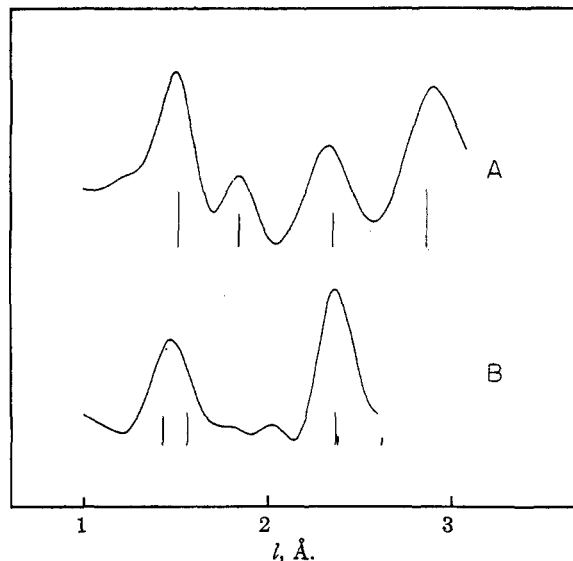

Fig. 1.—Radial distribution function, $D(l)$ vs. l: Curve A, thiophosphoryl fluoride; Curve B, sulfuryl fluoride. The vertical lines represent the internuclear distances found.

The parameter β was assumed to be 100° for all these curves. This is roughly the value found for the chlorine–sulfur–chlorine angle in sulfuryl and thionyl chlorides, and the qualitative and quantitative character of the theoretical curves is quite insensitive to variations in the value of this parameter. Some of these curves are shown in Fig. 2. Of these curves only the two with $\rho_1 = 1.56/1.43$ and $\rho_2 = 2.36/1.43$ or 2.38/1.43 are in agreement with the appearance of the photographs. Curves were then calculated for models with these values of ρ_1 and ρ_2 with $\beta = 90$ and 110°. The curves with $\beta = 90°$ are unsatisfactory because feature b disappears while for $\beta = 110°$ the fifth maximum is too low. This is illustrated by curves E_1 and E_2 of Fig. 2.

Quantitative comparison of the photographs with the curves for $\rho_1 = 1.56/1.43$, $\beta = 100°$ and $\rho_2 = 2.36/1.43$ and 2.38/1.43 is made in Table I, columns 7 and 9. The agreement is quite satisfactory. The final results for the structure of sulfuryl fluoride are

S–F = 1.56 ± 0.02 Å.   ∠F–S–O = 105 ± 2°
S–O = 1.43 ± 0.02 Å.   ∠F–S–F = 100 ± 8°
F–O = 2.37 ± 0.02 Å.   ∠O–S–O = 130 ± 10°

Thiophosphoryl Fluoride.—The photographs of thiophosphoryl fluoride were exceptionally clear, showing nine rings. The first and third maxima appear weaker than the second maximum, and the fifth maximum is weaker than the
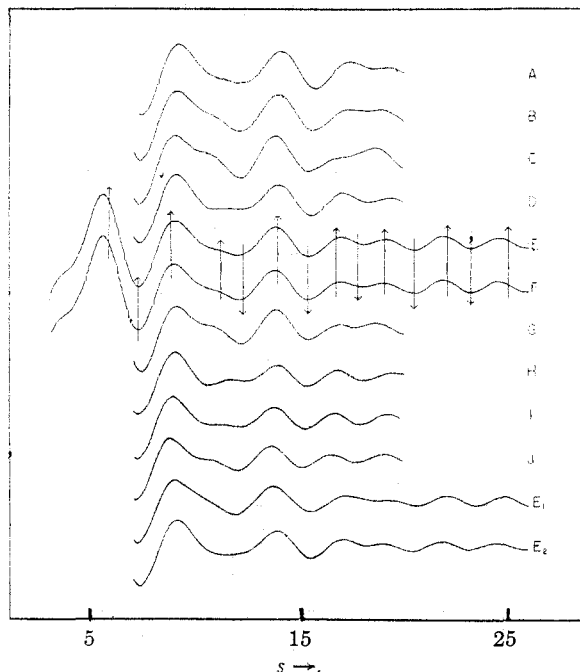
Fig. 2.—Theoretical scattering curves for sulfuryl fluoride:

Curve A, $\rho_1 = 1.52/1.43$; $\rho_2 = 2.32/1.43$; and $\beta = 100°$
Curve B,   2.36/1.43   100°
Curve C,   2.40/1.43   100°
Curve D, $\rho_1 = 1.56/1.43$ 2.32/1.43   100°
Curve E,   2.36/1.43   100°
Curve F,   2.38/1.43   100°
Curve G,   2.40/1.43   100°
Curve H, $\rho_1 = 1.60/1.43$ 2.32/1.43   100°
Curve I,   2.36/1.43   100°
Curve J,   2.40/1.43   100°
Curve E_1, $\rho_1 = 1.56/1.43$ 2.36/1.43   110°
Curve E_2,   2.36/1.43   90°

fourth and sixth maxima. The fourth minimum is deeper than the third minimum and the sixth minimum is slightly deeper than the fifth minimum. The visually estimated relative intensities are given in Table II along with the values of $S_{obs.}$.

The radial distribution function calculated according to (1), with the coefficients C_n, given in column 4 of Table II, has four maxima (see curve A, Fig. 1) at 1.50, 1.85, 2.33, and 2.90 Å. These correspond to the four distances, phosphorus–fluorine, phosphorus–sulfur, fluorine–fluorine and fluorine–sulfur. The fluorine–phosphorus–fluorine and fluorine–phosphorus–sulfur angles computed from these distances are 100 and 118°, respectively.

If this molecule has the symmetry C_{3v}, two structural parameters determine the shapes of

TABLE II

Max.	Min.	I_0	C_n	s_0	$s_0{}^a$	s_0/s_0
1		5	2	2.95	..	..
	2	−9	−5	3.62	..	..
2		10	6	5.06	4.84	(0.957)[b]
	3	−2	−2	5.84	6.28	(1.075)
3		3	3	7.01	6.89	(0.983)
	4	−8	−9	7.67	7.71	1.005
4		8	9	9.17	9.09	0.991
	5	−5	−7	10.15	10.34	1.019
5		4	6	11.46	11.35	0.990
	6	−6	−9	12.36	12.42	1.005
6		6	10	13.89	13.73	0.988
	7	−4	−7	15.57	15.70	1.008
7		4	7	17.67	17.65	0.999
	8	−3	−5	19.36	19.13	·0.988
8		3	5	21.73	22.00	1.013
	9	−1	−2	23.25	23.45	1.009
9		1	2	25.19	24.90	0.988

Average of 12 features 1.001 ± 0.010

[a] From model with $\dfrac{P - F}{P - S} = \dfrac{1.52}{1.85}$ and $\angle \text{F-P-F} = 99°$.

[b] Values in parentheses omitted from average because of unreliability of measurements.
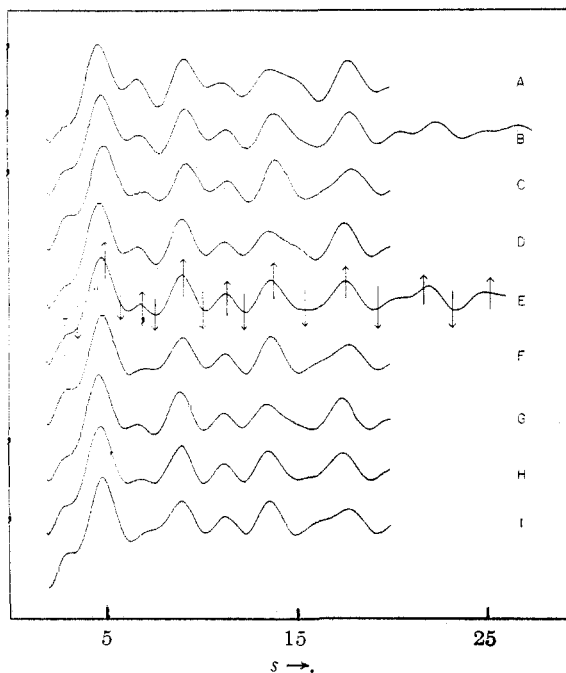

Fig. 3.—Theoretical scattering curves for thiophosphoryl fluoride.

Curve A, $\rho = 1.48/1.85$ $\alpha = $ 96°
Curve B,   99°
Curve C,   102°
Curve D, $\rho = 1.52/1.85$ 96°
Curve E,   99°
Curve F,   102°
Curve G, $\rho = 1.54/1.85$ 96°
Curve H,   99°
Curve I,   102°

TABLE III

	P-F	P-Cl	P-Y	X-P-X	Reference
PF₃	1.52 ± 0.02 Å.			104 ± 4°	12 and 8
OPF₃	1.52 ± 0.02		1.56 ± 0.02 Å.	107 ± 2°	2
OPF₂Cl	1.51 ± 0.02	2.01 ± 0.02 Å.	1.55 ± 0.03	106 ± 3°	2
OPFCl₂	1.50 ± 0.03	2.02 ± 0.02	1.54 ± 0.03	106 ± 3°	2
OPCl₃	....	2.02 ± 0.02	(1.58)ᵃ	106 ± 1°	2
PCl₃	....	2.00 ± 0.02		101 ± 2°	12 and 8
SPF₃	1.51 ± 0.02		1.85 ± 0.02	99.5 ± 2°	This research
SPCl₃		2.01 ± 0.02	1.94 ± 0.03	107 ± 3°	4

ᵃ This distance was assumed.

appropriate models and the form of the theoretical intensity curves. These parameters are conveniently taken as the ratio ρ of the phosphorus–fluorine to the phosphorus–sulfur distance, and α the fluorine–phosphorus–fluorine angle.

Curves were calculated for eighteen models, in which α was varied from 90–108° and ρ was varied from 1.54/1.85 to 1.46/1.85. A selection of these curves is shown in Fig. 3. All models with $96° \geqslant \alpha \geqslant 102°$ could be eliminated because the appearance of the third maximum on the curves is not that of the photographs and they show an asymmetry on either the outer side of the sixth maximum or the inner side of the seventh maximum while on the photographs these maxima appear quite symmetrical. The model with $\alpha = 99°$ and $\rho = 1.54/1.85$ is unsatisfactory because its fourth minimum is not deeper than its third and the sixth minimum is not deeper than the fifth. The curves for models with $\rho = 1.50/1.85$ and $\alpha = 99°$ show a shelf on the inner side of the ninth maximum and are unsatisfactory for this reason.

The curve calculated for the model $\rho = 1.52/1.85$ and $\alpha = 99°$ is in good qualitative agreement with the photographs. The quantitative comparison of this model with the photographs is shown in Table II. The final results for the structure of thiophosphoryl fluoride are P-F = 1.51 ± 0.02 Å., P-S = 1.85 ± 0.02 Å., $\angle$ F-P-F = 99.5 ± 2°, and $\angle$ F-P-S = 118 ± 2°.

Discussion.—Table III presents a summary of the structures found for molecules of the type X₃PY.

The distances predicted by the covalent radius table[13] are P-F (single bond) = 1.74 Å., P-Cl (single bond) = 2.09 Å., P-O (double bond) = 1.57 Å., and P-S (double bond) = 1.95 Å. The structure of thiophosphoryl fluoride presents two interesting differences from the structures

(12) L. O. Brockway and F. T. Wall, THIS JOURNAL, **56**, 2373 (1934).

(13) L. Pauling and L. O. Brockway, *ibid.*, **59**, 1223 (1937).

of the other molecules in the group that have been studied, a decrease of 0.09 Å. in the phosphorus–sulfur distance and a small fluorine–phosphorus–fluorine angle.

An explanation for the first of these differences may be found from a consideration of the various resonating valence bond structures that may be written for molecules of this type.
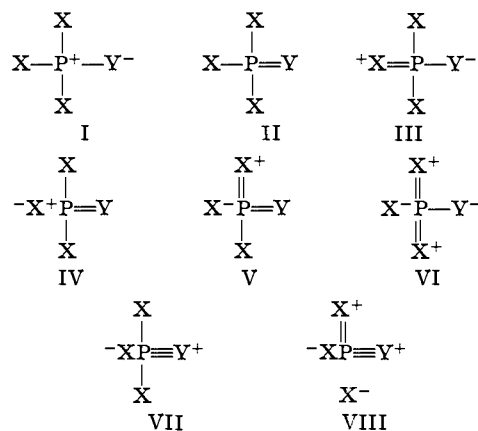
The much greater shortening observed for the phosphorus–fluorine distance, 0.22 Å., than for the phosphorus–chlorine distance, 0.08 Å., has been explained by the assumption of a larger contribution of structures IV–VIII to the resultant structure of molecules containing fluorine, made possible by the larger electronegativity[14] of fluorine. Since the electronegativity of oxygen is so much larger than the electronegativity of phosphorus and sulfur, structures VII and VIII are unimportant in the molecules X₃PO. Thus we interpret the extra shortening of the phosphorus–sulfur bond in thiophosphoryl fluoride as due to considerable triple bond character made possible by the large electronegativity of fluorine and the small difference in the electronegativity between phosphorus and sulfur.

Although several explanations for the small fluorine–phosphorus–fluorine angle in thiophos-

(14) L. O. Brockway, *J. Phys. Chem.*, **41**, 185 (1937).

phoryl fluoride present themselves, a satisfactory one cannot be advanced until more data have been acquired.

The sulfur–fluorine distance in sulfuryl fluoride, 1.56 Å., is 0.12 Å. less than the single bond distance predicted by the covalent radius table.[13] This shortening is not as great as is observed in the fluorine derivatives of phosphorus. A similar situation obtains for the corresponding chlorine compounds of sulfur and phosphorus.

It is of interest to note that, although there is much more shortening in the sulfur–halogen bond in sulfuryl fluoride than in sulfuryl chloride, the sulfur–oxygen distance in sulfuryl fluoride, 1.43 Å., is just that found for this distance in sulfur dioxide,[15] sulfur trioxide,[3] and sulfuryl chloride.[3]

In conclusion it should be remarked that the

(15) V. Schomaker and D. P. Stevenson, to be published.

large uncertainty in the fluorine–sulfur–fluorine angle, ±8°, introduces an uncertainty of less than 0.1 E. U. into the calculation of the rotational entropy from the structure of the molecule.

Summary

The structures of sulfuryl fluoride and thiophosphoryl fluoride have been investigated by the electron diffraction technique. The interatomic distances and bond angles are: for sulfuryl fluoride, S–F = 1.56 ± 0.02 Å., S–O = 1.43 ± 0.02 Å., $\angle$ F–S–O = 105 ± 2°, and $\angle$ F–S–F = 100 ± 10°; and for thiophosphoryl fluoride, P–F = 1.51 ± 0.02 Å., P–S = 1.85 ± 0.02 Å., $\angle$ F–P–F = 99.5 ± 2°, and $\angle$ F–P–S = 118 ± 2°. The relationship between the structures found and the resonating valence bond structures is briefly discussed.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NEW YORK UNIVERSITY]

Solubility of Barium Iodate Monohydrate in Solutions of Uni-Univalent Electrolytes at 25°, and the Calculation of the Dissociation Constant of Iodic Acid from Solubility Data[1]

BY SOLOMON NAIDICH AND JOHN E. RICCI[2]

Barium iodate was one of the first salts to be used in the testing of theories of solutions of electrolytes through the effect of added electrolytes on the solubility of difficultly soluble salts. Such measurements for barium iodate were made by Harkins and Winninghoff,[3] in barium nitrate, potassium nitrate and potassium iodate solutions; by Polessitskii[4] in potassium nitrate and calcium nitrate solutions up to very high concentrations; and by Macdougall and Davies,[5] in dilute solutions of potassium chloride, nitrate, chlorate and perchlorate, and of calcium chloride.

In the present work, at the expense of repeating some of the measurements already found in the literature, it was decided to attempt to calculate the dissociation constant of iodic acid through the relative effects on the solubility of barium iodate

(1) Presented before the Division of Physical and Inorganic Chemistry, American Chemical Society, at Boston, September, 1939.

(2) The experimental part of this paper is taken from a thesis submitted by Mr. S. Naidich to the Graduate School of New York University in partial fulfilment of the requirements for the degree of Master of Science, June, 1939.

(3) Harkins and Winninghoff, THIS JOURNAL, 33, 1827 (1911).

(4) Polessitskii, Compt. rend. l'acad. sci., U. R. S. S., 14, 193 (1935).

(5) Macdougall and Davies, J. Chem. Soc., 1416 (1935).

of the simple electrolyte potassium chloride and of the corresponding acid, hydrochloric, and, similarly, through the relative effects of the pair potassium nitrate and nitric acid on the same solubility. Measurements are therefore presented giving the effect of these four uni-univalent electrolytes on the solubility of $Ba(IO_3)_2 \cdot H_2O$ at 25°, calculation of the various Debye–Hückel parameters for the mean activity coefficient of $Ba(IO_3)_2 \cdot H_2O$ in these solutions, and, finally, calculation of the dissociation constant of iodic acid, based on the observed solubility data and certain assumptions to be stated.

Experimental

$Ba(IO_3)_2 \cdot H_2O$, c. p. grade, was washed eight to ten times with distilled water, the smaller particles being removed by a regulated process of sedimentation and decantation. Analysis of the product (dried at about 100°) before use, gave 96.5% $Ba(IO_3)_2$ as compared with the theoretical figure of 96.43% for the monohydrate. The analytical method here and in the solubility determinations themselves was the iodometric titration of the iodate by means of 0.05 N sodium thiosulfate solution, previously standardized against pure potassium iodate. The procedure, involving the use of weight burets, was standard; blanks were taken to correct for any iodate in the potassium iodide