

Biomimetic Reduction of Sulfuric Acid

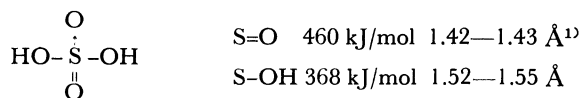
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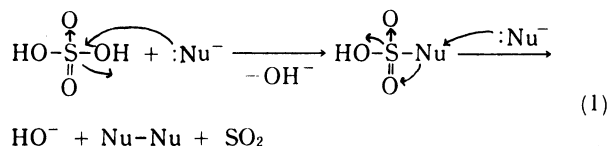
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Sulfuric acid and sodium sulfate were readily reduced to elemental sulfur and hydrogen sulfide upon treatment with a mixture of either one of polyphosphoric acid derivatives, PPE, PPA, and P_4O_{10} , which can form a mixed anhydride having $-P-O-S-$ linkage, and iodide or thiol. Sulfur dioxide, which is undoubtedly one of important intermediates, was trapped by *p*-tolyllithium to afford *p*-toluenesulfinic acid which was converted to *p*-tolyl methyl sulfone upon treatment with methyl iodide, though the yield was low. Sulfur trioxide which has been postulated as the key intermediate in the biological reduction of inorganic sulfate, was also trapped by mesitylene to give mesitylenesulfonic acid in a high yield. The reduction of sulfate to elemental sulfur and hydrogen sulfide is considered to proceed through the course which resembles the biological reaction path involved in the assimilatory metabolism of inorganic sulfate in microorganisms and plants.

Inorganic sulfate which is in the highest oxidative state of sulfur atom is one of the most inert species toward any reducing agent among the naturally occurring sulfur compounds, and hence clean reduction of inorganic sulfate by any chemical means under mild conditions has been considered to be most difficult.



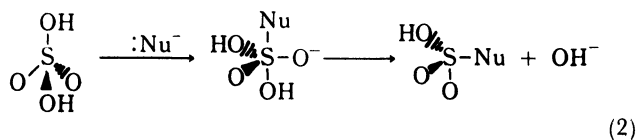
The deoxygenative reduction of sulfuric acid may proceed stepwise *via* an initial nucleophilic displacement of OH group of sulfuric acid by a leaving group, followed by subsequent nucleophilic attack on the leaving group by a second nucleophile as shown in Eq. 1.



However, such a simple nucleophilic replacement of OH group of sulfuric acid does not seem to proceed readily, due mainly to the following reasons.

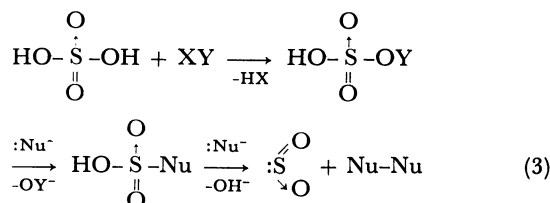
a) Sulfuric acid is a very strong acid which can dissociate so readily to divalent sulfate ion by supplying two protons to the attacking nucleophile that the nucleophile eventually loses the nucleophilic reducing ability due to the protonation to the lone electron pair of the nucleophile. Divalent sulfate ion, bearing two negative charge, may also no longer readily receive nucleophilic attack at its central sulfur atom due to the charge repulsion.

b) Even undissociated sulfuric acid would resist the nucleophilic attack, due to the steric hindrance and electronic repulsion by four oxygen atoms bound to the central sulfur, while three electronegative oxygens must be placed in the unfavorable equatorial position in the transition state of the substitution as shown in Eq. 2.



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c) The leaving ability of OH group is rather poor in most nucleophilic substitution reactions. Therefore, it would be necessary to substitute proton by some other electron-withdrawing group by treatment with some condensing reagent XY to activate the central sulfur to receive nucleophilic attack as shown in Eq. 3.



Meanwhile, many plants, microorganisms are known to reduce inorganic sulfate to some sulfur-containing amino acids as shown below²⁾ *via* sulfite and sulfide in the assimilatory metabolism. The biological reduction of sulfate consists of the following two key steps, *i.e.* the conversion of sulfate to a mixed anhydride, APS or PAPS, to activate sulfate, and the subsequent nucleophilic attack of a certain protein-thiol on the sulfur atom of APS or PAPS to generate the protein-bound thiosulfate. Then, the sulfonyl sulfur of the protein-bound thiosulfate can be easily displaced by other mercapto group in the enzyme to give sulfite which is ultimately reduced to hydrogen sulfide, or the sulfonyl group of the protein-bound thiosulfate is reduced by thiosulfate reductase to form R^1SS^- or R^2SS^- . This paper describes the first successful chemical model reactions for the assimilatory biological reduction of inorganic sulfate.

Results and Discussion

Since the essential part of ATP which takes part in the biological reduction of sulfate is the triphosphate linkage, polyphosphoric acid (PPA), ethyl polyphosphate (PPE),³⁾ and tetraphosphorus decaoxide are considered to be used as ATP model compounds. When sulfuric acid was added to either one of these polyphosphoric acid derivatives, we observed mild evolution of heat, probably

due to the formation of $-\overset{\text{O}}{\underset{\text{O}}{\text{P}}}-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-$ bond, which is the essential part of the mixed anhydride. Iodide is known

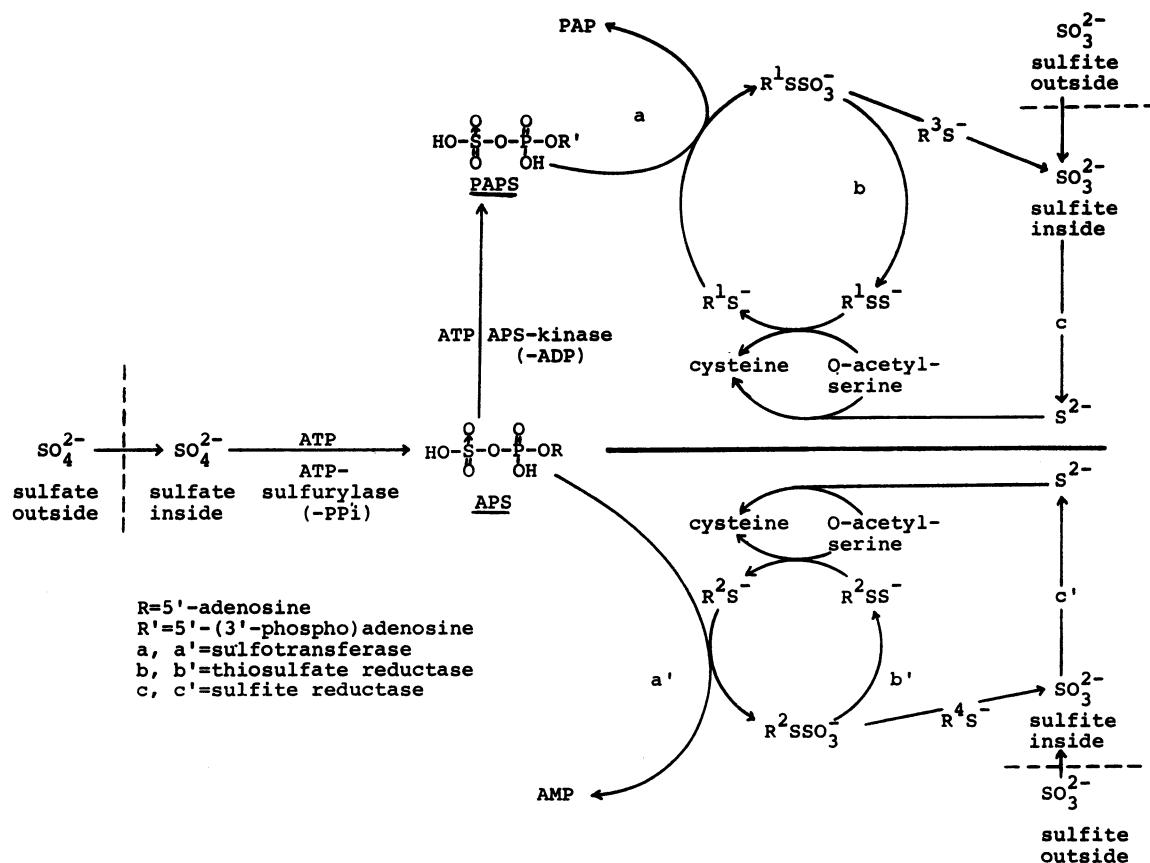
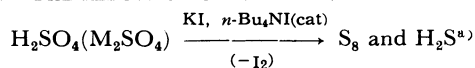


Fig. 1. Pathways of assimilatory sulfate reduction.

TABLE. THE REDUCTION OF SULFURIC ACID AND SULFATE



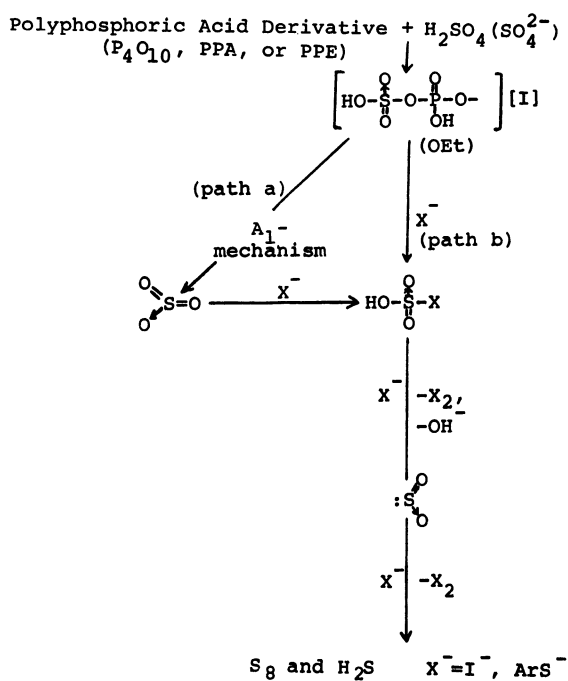
Run	Polyphosphoric acid derivative	Solvent	Temp °C	Time h	Yields/%		
					(A) S ₈	(B) ^a S ₈	H ₂ S
1	P ₄ O ₁₀	Acetonitrile	42—45	10	17	—	—
2	PPE	Chloroform	25	7	4—10	—	—
3	PPA	Sulfolane	75	8	58	—	—
4 ^b	PPA	Sulfolane	75	17	15	—	—
5 ^c	PPA	Sulfolane	70—73	7	40—44	—	—
A	PPE	Acetonitrile	25	5	23	0	Trace
B	PPA	Sulfolane	75	4	42	Trace	15
C ^c	PPA	Sulfolane	75	8	10	0	Trace
6 ^d	PPA	Sulfolane	75	8	0	—	—

a) Hydrogen sulfide was isolated as *N,N'*-dicyclohexylthiourea in the trapping experiment with DCC. When N₂ gas was bubbled into the reaction mixture(A) and the exhausted gas was introduced into a benzene solution of DCC(B).

b) Na₂SO₄ was used. c) (*n*-Bu₃NEt)₂SO₄ was used. d) No presence of H₂SO₄.

to be a facile reducing agent which can reduce oxidized organosulfur derivatives such as sulfoxides,⁴⁾ sulfinic acids,⁵⁾ sulfonyl halides,⁶⁾ thiosulfonic *S*-esters,⁷⁾ and sulfonic acids⁸⁾ to divalent organosulfur compounds, forming iodine, in a similar manner as in the case with thiols⁹⁾ which are readily oxidized to disulfides and play the most important role in the reduction of sulfate in microorganisms and plants. Although it is desirable to use thiols in order to mimic the biological reduction of sulfate, since iodide may not be present in nature,

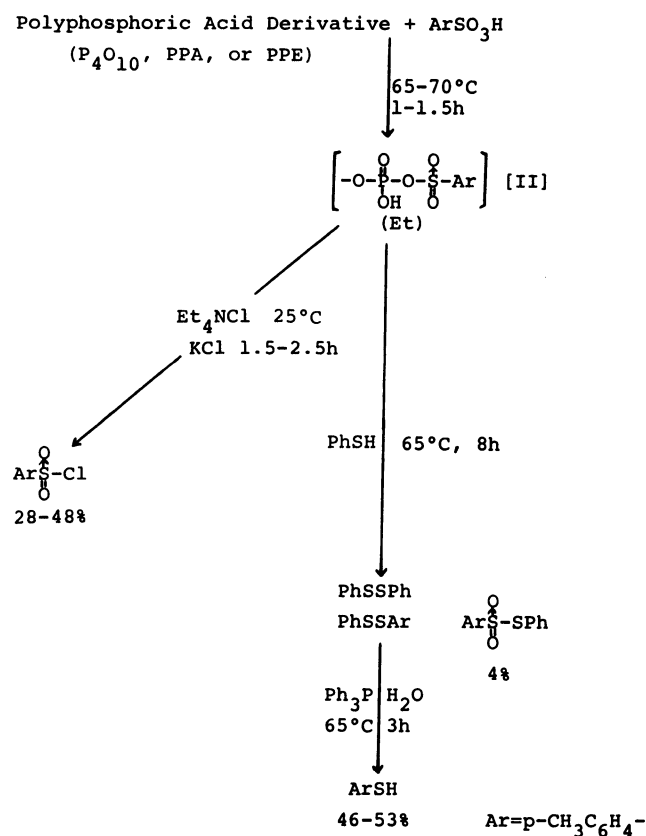
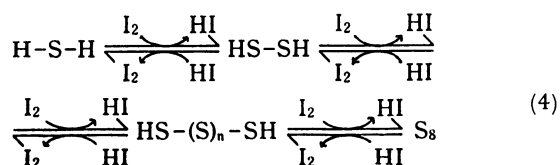
iodide is a little more reactive than thiols and the reaction is conveniently followed. Meanwhile, many reactive thiols can often form mixed disulfides or polysulfides which are not readily separated for characterization, and hence iodide was used for the reduction at first for a detailed observation of the simple reduction and then thiols were used. The chemical behavior of iodide in the reduction is very similar to that of thiols. Sulfuric acid is, however, very inert and not reduced by iodide or thiols alone. Only in the presence of such condensing



Scheme 1.

agents as polyphosphoric acid derivatives, sulfate was reduced to sulfide with either iodide or thiols. The solvents used for the reactions with PPA and P_4O_{10} were dry sulfolane and acetonitrile respectively, since both solvents can readily dissolve these polyphosphoric acid derivatives, however, common polar aprotic solvent such as acetonitrile or chloroform can also be used in the reaction with PPE because of its high solubility in these solvents.

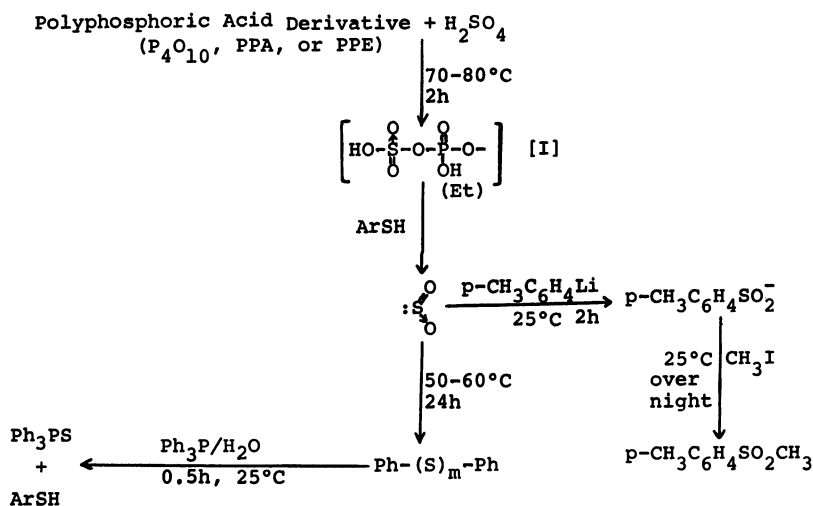
The results obtained in reduction of sulfuric acid are shown in Table 1. The products were elemental sulfur and hydrogen sulfide. Under acidic conditions, thiol group (*i.e.* hydrogen sulfide) and polysulfide (*i.e.* elemental sulfur) are in an equilibrium as shown in Eq. 4 (generally, thiol is oxidized by iodine in the presence of a base, *e.g.* pyridine or amine). Therefore the reduction products obtained were a mixture of hydrogen sulfide and elemental sulfur. The rather low yields of the reduction products are mainly due to the difficulty of purification and isolation of these products from the reaction mixture. In the absence of $n\text{-Bu}_4\text{N}^+\text{I}^-$, the yields of the reduction products were markedly decreased. In the runs 1, 2, 3, 4, and 5, the reduction to sulfur was carried out in one flask, whereas, in the runs A, B, and C, while the reduction was carried out in one flask, nitrogen gas was introduced into the flask to drive out evolving hydrogen sulfide into another flask which contained a dry benzene solution of DCC that can trap hydrogen sulfide to afford the thiourea derivative. Generally, when iodide ion was added into a mixture of sulfuric acid and any one of the polyphosphoric acid

Fig. 2. Reduction of ArSO_3H to ArSH by polyphosphoric acid derivative/PhSH.

derivatives, the formation of hydrogen sulfide gas was easily detected.

Both elemental sulfur and the thiourea can be readily identified by comparison with the authentic samples (TLC, mp).

Inspection of the data in the Table reveals that PPA is the best model substrate for ATP, and gave sulfur and hydrogen sulfide in the highest yields. The rather low yields of reduction species in the reaction with either P_4O_{10} or PPE are believed to be due to the subsequent reaction between hydrogen sulfide formed and P_4O_{10} , which is a strong proton acceptor, or PPE which is an effective alkylating agent. The postulated mechanism is shown in Scheme 1. In this Scheme, [I] is believed to be the key intermediate in the presence of excess of any polyphosphoric acid derivative. Sulfite is also one of the intermediate, which is eventually reduced to elemental sulfur in a high yield in the reaction with a mixture of PPA and KI under similar conditions. The formation of intermediate [I] may be supported by a trapping experiment described in the reduction of sulfonic acid with the same system.¹⁰⁾ Namely, when chloride ion was added into the reaction mixture of polyphosphoric acid derivative and *p*-toluenesulfonic acid, *p*-toluenesulfonyl chloride was obtained as Fig. 2. However, isolation of chlorosulfuric acid in the reaction of the intermediate [I] with chloride anion was not achieved because of its rather high reactivity. Thus, only in the reaction of arenesulfonic acid we could isolate the sulfonyl chloride by treating the intermediate [II] with chloride.



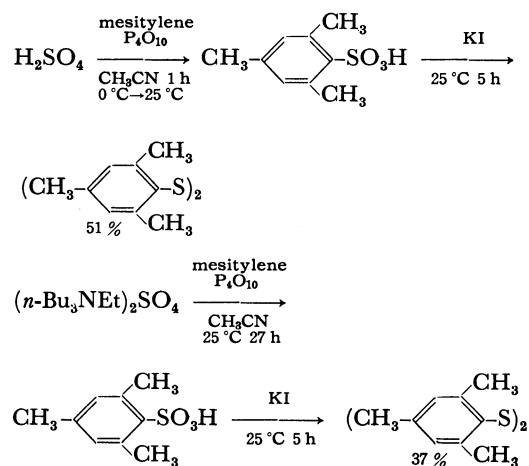
Scheme 2.

Sulfur dioxide is also an intermediate; however, it is so readily reduced by hydrogen iodide that it is difficult to trap SO₂ when iodide ion is used as the reducing agent. Instead of using iodide, excess thiophenol can be added as the reducing agent into the mixture of polyphosphoric acid derivative and sulfuric acid. Thus, sulfuric acid was reduced by thiophenol to afford diphenyl polysulfide of which middle sulfur atoms are derived from sulfuric acid. The polysulfide was then converted to thiophenol and triphenylphosphine sulfide upon of triphenylphosphine. Though the yield of the triphenylphosphine sulfide was low (2%), the combined sulfur atom of triphenylphosphine sulfide is obviously derived from sulfuric acid. The rather low yield of divalent sulfur is due to the fast reaction of thiophenol and polyphosphoric acid derivative as compared to the reduction of compound [I] by thiophenol.

Since thiophenol is a mild reducing agent as compared to hydrogen iodide, sulfur dioxide was successfully trapped by *p*-tolyllithium, when SO₂ gas formed was driven out into an ether solution of *p*-tolyllithium to afford *p*-toluenesulfinate which was then converted to the sulfone by treating with methyl iodide, though the yield of the sulfone was poor (≈1%). Although the yields of the reduction products are not high, the successful reduction of sulfuric acid and sulfate to sulfides in this biomimetic reduction with polyphosphoric acid derivatives with iodide or thiols, and the trapping of sulfur dioxide under mild conditions would be the first reported experiment which can successfully mimic the biological assimilatory sulfate reduction. In the reduction, two path (a and b) are conceivable for the reaction of compound [I] with nucleophile (I⁻, PhSH). While path b may be unfavorable due to the stereo-electronic repulsion between the nucleophile and negative oxygen poles of bulky sulfate group of [I] at the transition state of the S_N2 reaction on the sulfur atom of [I], path a would be quite likely since hydrogen bound to the oxygen atom of [I] is extremely acidic.

Thus, 1,2-elimination reaction of [I] to form sulfur trioxide and phosphoric acid by E1cb process should take place quite readily.¹¹⁾ Sulfur trioxide thus formed may react with iodide or arenethiol to afford iodosulfuric

acid, or thiosulfuric acid either of which is considered to be subsequently reduced readily with iodide or thiols to afford sulfite. Sulfite ion (*i.e.* SO₂ in acidic conditions) is reduced further very readily with these systems to sulfide.¹²⁾ Actually, in one of our trapping experiments, sulfur trioxide was nicely trapped by mesitylene to give mesitylenesulfonic acid in the reaction of tetraphosphorus decaoxide and sulfuric acid under acidic conditions and also in the reaction between tetraphosphorus decaoxide and bis(tributylethylammonium) sulfate,



which are both neutral respectively. In a blank experiment, in the absence of tetraphosphorus decaoxide, *i.e.* the mixture of mesitylene and sulfuric acid, or the mixture of mesitylene and bis(tributylethylammonium) sulfate under similar conditions, the corresponding mesitylenesulfonic acid was not obtained. Earlier, Eiki and Tagaki¹³⁾ and Benkovic and Hevey¹⁴⁾ reported independently that the nucleophilic substitution of phenyl phosphatosulfate (PPS), a APS or PAPS model compound, similar to [I] in our experiment, by OH⁻ ion proceeded sluggishly, however, hydrolysis of PPS easily took place in acidic media or in the presence of some metal ions in aprotic solvents such as DMF. These results together with our results suggest clearly the elimination-addition mechanism involving the formation of sulfur trioxide in the acidic media (path a) as shown Scheme 1.

Experimental

Materials. PPA, potassium iodide, mesitylene, sulfuric acid, tributylamine, diethyl sulfate, tetraphosphorus decaoxide, and dicyclohexylcarbodiimide are all from Wako Chemicals Co., tetrabutylammonium iodide was from Tokyo Kasei Co., and sodium sulfite was obtained from Kanto Kagaku Co.

Ethyl Polyphosphate. Ethyl polyphosphate was prepared by a known method.¹⁵⁾ Tetraphosphorus decaoxide, 150 g, was added into a solution of 300 ml of dry ether and 150 ml of dry chloroform. The mixture was refluxed for 4 d under N₂ (bath temperature 50 °C). As the reaction proceeded, the crystalline P₄O₁₀ faded away to give a homogeneous liquid. After completion of this reaction, the liquid phase was decanted into a flask in a dry box. Then the solution was evaporated to a colorless syrup. The residue was then dried by vacuum pump for 36 h at 40 °C. A colorless syrupy (hard) ester which is very sensitive to moisture, was obtained. NMR (CDCl₃) δ = 1.9—1.5 (3H, m) and 4.2—5.0 (2H, m).

Reduction of Sulfuric Acid with PPA/KI/n-Bu₄N⁺I⁻ (cat) System to Sulfide.

Polyphosphoric acid, 10 g (29.7 mmol, M.W. = 338) and 4.93 g (29.7 mmol) of potassium iodide were added into 6 ml of dry sulfolane. Then, 300 mg (2.97 mmol) of sulfuric acid was added into this mixture, into which finally 184 mg (0.5 mmol) of tetrabutylammonium iodide was added. The reaction was carried out for 8 h at 75 °C with stirring under nitrogen atmosphere. The odor of hydrogen sulfide was clearly detected. After the reaction, 10 ml of water was added and the mixture was heated under similar conditions for 0.5 h in order to hydrolyze excess PPA. The reaction mixture was poured into benzene which solution was washed with water for 3 times, dried (MgSO₄), filtrated and the filtrate was evaporated. The residue was subjected to TLC (MERCK, silica gel type-60), separated with benzene to exclude iodine, then 55 mg of sulfur was obtained and identified by comparison with authentic sulfur (TLC R_f = 0.7, eluent; benzene) mp 112—114 °C (lit.¹⁶⁾ 115 °C). After recrystallization with a mixture of benzene and hexane, the yield of sulfur was 58%.

Hydrogen Sulfide Trapping in PPA/KI/n-Bu₄N⁺I⁻ (cat) System. Reactor A: PPA (10 g) and 4.93 g (29.7 mmol) of potassium iodide were added into 6 ml of dry sulfolane. Then, 300 mg of sulfuric acid was added and finally 184 mg (0.5 mmol) of tetrabutylammonium iodide was added into this mixture.

Reaction B: Dicyclohexylcarbodiimide 18.4 g (9 mmol) was dissolved in 10 ml of dry benzene in a flask which was equipped with empty balloon.

Reactor B was jointed reactor A with a glass tube. The content in reactor A was stirred and heated for 4 h at 75 °C under slow flowing of nitrogen gas. While the reaction mixture in reactor B was stirred at room temperature, nitrogen and hydrogen sulfide were introduced into the reactor B. After the reaction, 10 ml of water was added to the reactor A and the mixture was heated under similar conditions for 1 h. The reaction mixture in reactor A was poured into benzene and washed with water for 3 times, dried (MgSO₄), filtrated and evaporated. The residue was separated by TLC with benzene to give sulfur. From the reactor A, 40 mg of sulfur was obtained. Yield 42%. In a separative experiment, 10 ml of water was added into the reactor B to quench any excess of dicyclohexylcarbodiimide to urea and the mixture was kept standing for a few hours. The mixture was poured into benzene which solution was washed with water, dried (MgSO₄), and benzene was evaporated. The residue was separated through silica-gel column with chloroform. *N,N'*-Dicyclohexylthiourea (103 mg, yield 15%), TLC (eluent; CHCl₃) R_f = 0.3—0.4; IR

(KBr) 1540, 3275, 1490 and 1220 cm⁻¹; mp 182—184 °C (lit.¹⁷⁾ 182—182.5 °C). A similar procedure with a similar molar ratio was used in the reduction of sodium sulfate in PPA system.

Trapping of Sulfur Trioxide in P₄O₁₀ by Mesitylene I.

Tetraphosphorus decaoxide, 2100 mg (15 mmol), was added into 6 ml of dry acetonitrile into which 2 ml of mesitylene was then added. The mixture was cooled down to 0 °C and 300 mg (2.97 mmol) of sulfuric acid was added into this mixture. The mixture was stirred for 1 h at room temperature (0 °C → 25 °C) under nitrogen atmosphere. Then, 4903 mg (29.7 mmol) of potassium iodide, 184 mg (0.5 mmol) of tetrabutylammonium iodide and 4 ml of dry acetonitrile were added into this reaction mixture which was stirred for 5 h at room temperature under nitrogen. Since the isolation of mesitylenesulfonic acid is difficult in our system, the sulfonic acid was reduced to the disulfide with P₄O₁₀/KI system under mild conditions. Thus, mesitylenesulfonic acid was converted to dimesityl disulfide. After the reaction, 10 ml of water was added and the mixture was stirred for 1 h. The reaction mixture was poured into benzene which solution was washed with water for three times, 0.5 mol dm⁻³ of Na₂S₂O₃, once, again with water and dried (MgSO₄).

Dimesityl disulfide, which was derived from mesitylenesulfonic acid, was obtained in ca. 50% by GLC (OV-1, 1 m glass column). Authentic dimesityl disulfide was obtained by reducing mesitylenesulfonyl chloride with lithium aluminum hydride in dry diethyl ether for 1 h (0 °C → 25 °C) to mesitylenethiol which was oxidized further to dimesityl disulfide with iodine and pyridine at room temperature in 81% yield. Mp 124—125 °C (lit.¹⁸⁾ 125 °C).

Trapping of Sulfur Trioxide in P₄O₁₀ by Mesitylene II.

Bis(tributylethylammonium) sulfate, 588 mg (1.2 mmol) was dissolved in 5 ml of dry acetonitrile and 2 ml of mesitylene was added to this mixture. Then, 1200 mg (8.4 mmol) of tetraphosphorus decaoxide was added and the whole mixture was stirred for 27 h at room temperature under nitrogen atmosphere. Potassium iodide, 1860 mg (11.2 mmol), was added into this mixture, into which 5 ml of acetonitrile was added and the whole mixture was stirred for 5 h at room temperature. Bis(tributylethylammonium) sulfate obviously plays the role of phase-transfer catalyst. Then, 10 ml of water was added at 0 °C into the mixture which was stirred for 1 h at room temperature. The mixture was poured into benzene. The organic layer was separated and washed with water for three times, with 0.5 mol dm⁻³ of Na₂S₂O₃, once again with water once and dried (MgSO₄). Dimesityl disulfide was obtained in 37% yield (GLC, SE-30, 1 m glass column).

Trapping of Sulfonyl Group in ArSO₃H/P₄O₁₀/KCl System.

Tetraphosphorus decaoxide, 1600 mg (11.27 mmol), was added into 5 ml of dry acetonitrile, into which 381 mg (2 mmol) of *p*-toluenesulfonic acid was added. The mixture was heated and stirred for 1.5 h at 60—65 °C under nitrogen atmosphere. Then, 33 mg (0.2 mmol) of tetraethylammonium chloride, 746 mg (10 mmol) of potassium chloride were added into the reaction mixture at 0 °C and the mixture was stirred for 3 h at room temperature. After the reaction, the mixture was poured into benzene and washed with water for 3 times, then dried (MgSO₄). *p*-Toluenesulfonyl chloride was obtained in 48% yield (GLC), isolated in 43% yield. In the reaction with PPE, (PPE = 6 g, *p*-CH₃C₆H₄SO₃H·H₂O = 381 mg), the yield of *p*-toluenesulfonyl chloride was 28% under similar conditions.

Reduction of ArSO₃H to ArSH with PPA/Ar'SH System.

PPA, 6 g, and 381 mg of *p*-toluenesulfonic acid were added into 5 ml of dry sulfolane, which was stirred and heated for 1.5 h at 90 °C under nitrogen atmosphere (the initial step). Then 2 ml of thiophenol was added to this mixture, and the reaction

mixture was kept at 90 °C for 3 h (the latter step). After the reaction, 10 ml of water was added, then the mixture was poured into benzene, which solution was washed with water for three times, and dried (MgSO_4). A mixture of diphenyl disulfide and phenyl *p*-tolyl disulfide was obtained. Very little di-*p*-tolyl disulfide was formed. *S*-Phenyl *p*-toluenethiosulfonate was not formed. The mixture was purified by column chromatography through silica gel (eluent; benzene/hexane = 1/1 = v), and the disulfides obtained were converted to the corresponding thiols by the addition of the mixture of $\text{Ph}_3\text{P}/\text{H}_2\text{O}/\text{dioxane}$. The yield of *p*-toluenethiol was 53% (GLC). In the reduction with PPE (PPE = 7 g, $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ = 381 mg), both the initial step and the latter step required 1.5 h/65 °C and 8 h/65 °C respectively. The reaction mixture was then treated similarly and nearly a similar result was achieved. *p*-Toluenethiol 46%. *S*-Phenyl *p*-toluenethiosulfonate 4% mp 78–80 °C (lit.¹⁹ 78 °C).

Trapping of Sulfur Dioxide with *p*-Tolyl lithium. Reactor A (Step 1): PPE (10 g) was added to 800 mg (8 mmol) of sulfuric acid which reactor was heated and stirred at 80 °C for 1 h under nitrogen atmosphere.

Reactor B (Step 2): Lithium, 280 mg (40 mmol), was added into 5 ml of dry ether into which 5 ml of dry ether solution containing 5.1 g (30 mmol) of *p*-bromotoluene was added.²⁰ The mixture was stirred for a few hours under nitrogen atmosphere.

Step 3: Reactors A and B were jointed by a glass tube. Thiophenol, 3 ml, was added into the reactor A at room temperature. Then each solution in the reactors A and B was stirred for 2 h at room temperature under nitrogen atmosphere. After the reaction, the reaction mixture in reactors A and B was poured into water and washed with benzene for three times. The water was evaporated, the solution was concentrated, and excess methyl iodide was added into the mixture which was stirred over night ($\text{H}_2\text{O}/\text{EtOH}$ = 1/1 = v). *p*-Tolyl methyl sulfone, 11.4 mg, was obtained. Mp 84–85 °C (lit.²¹ 87 °C).

In the case of PPA, step 1 (PPA = 10 g, H_2SO_4 = 840 mg) 2 h/70–80 °C.

Step 2: (Li = 280 mg, $p\text{-CH}_3\text{C}_6\text{H}_4\text{Br}$ = 5130 mg, Et_2O = 15 ml) a few hours/r.t.

Step 3: The mixture of 2 ml of thiophenol and 6 ml of sulfolane was added to reactor A and was stirred for 2 h at room temperature. The similar procedure and reaction conditions were used. *p*-Tolyl methyl sulfone, 10 mg, was obtained.

Reduction of Sulfuric Acid by Thiophenol in PPA. A mixture of PPA (10 g) and 0.8 g of sulfuric acid was heated under stirring for 2 h at 80 °C in nitrogen atmosphere. Then, 5 ml of thiophenol was added into this mixture which was stirred for 24 h at 50–60 °C. After the reaction, 10 ml of water was added and the mixture was poured into benzene, which solution was washed with water for three times, and dried (MgSO_4).

Triphenylphosphine 786 mg (3 mmol) was then added to this benzene solution, and 46 mg of triphenylphosphine sulfide was obtained. Triphenylphosphine sulfide was not obtained at all in the reaction of triphenylphosphine and diphenyl disulfide or thiophenol. Sulfur and diaryl polysulfide are known to be desulfurized by triphenylphosphine to give only triphenylphosphine sulfide, and arenethiol, respectively.

Triphenylphosphine sulfide mp 162–163 °C (lit.²² 162–164 °C).

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