

OXYGEN ISOTOPIC STUDY OF THE OXIDATION OF SO₂ BY H₂O₂ IN THE ATMOSPHERE

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INTRODUCTION

Considerable interest has been shown in the possibility of using oxygen isotopy to elucidate the role of H₂O₂ in the oxidation of SO₂ to sulfates in the atmosphere (1). The potential importance of H₂O₂ lies in the view that aqueous-phase oxidation of SO₂ to H₂SO₄ probably accounts for a major fraction of the observed SO₄²⁻ in the precipitation occurring in the northeastern United States. The key reactants responsible for this oxidation are not well known, although a large number of possible catalysts and oxidants exist in the atmosphere, including carbon, transition metal ions, hydroxyl and organic free radicals, hydrogen peroxide and ozone. Of these, the last two are the only ones believed to be present in sufficient quantity to produce the observed amounts of SO₄²⁻ in wet deposition. It is quite possible that the atmospheric oxidation of SO₂ is limited by the availability of one or both of these oxidants, rather than by the availability of SO₂ itself. It is therefore important to determine if indeed H₂O₂ has a pivotal role in acid formation and deposition from the atmosphere.

Oxygen isotopic studies are useful in distinguishing between the different oxidation mechanisms effective in the atmosphere. Laboratory simulation of several different atmospheric reaction sequences has shown that the oxygen isotope ratio in the product SO₄²⁻ is uniquely related to the reaction pathway followed in its formation (2). It may therefore be possible to determine if the atmospheric hydrogen peroxide is responsible for significant oxidation of SO₂ to sulfate, and if it is this oxidant that limits the aqueous-phase formation of sulfuric acid. The results of these studies could have significant implications for energy technology, particularly if they indicate that it may be more important to reduce the ambient concentrations of H₂O₂ than of SO₂.

In the 1981 JASON committee report to the U. S. Department of Energy (1), some recommendations for further research were based, at least in part, on our earlier work on SO₂ oxidation by H₂O₂ (3). In those studies the δ¹⁸O [deviation in parts per thousand (‰) of the ¹⁸O/¹⁶O ratio of the sample from that of the standard reference material, Standard Mean Ocean Water (SMOW)] of sulfates produced by H₂O₂ oxidation were significantly lower than the δ¹⁸O of sulfates found in rainwater. However, the δ¹⁸O of the reagent-grade H₂O₂ used in those experiments was not known. The results suggested the need for isotopic analysis of H₂O₂ in dilute solutions, and for a methodology whereby the δ¹⁸O values of H₂O₂, H₂O, and SO₄²⁻ in rainwater could be compared in order to assess the importance of H₂O₂ in the formation of sulfate-constituted acid rain.

EXPERIMENTAL

The plan of this investigation was to develop a method for the determination of the δ¹⁸O of H₂O₂ in dilute aqueous solutions (simulating rainwater); to prepare solutions of H₂O₂ of various ¹⁸O enrichments; to use the freshly prepared solutions of H₂O₂ to oxidize SO₂ to SO₄²⁻ for evaluation of the relationship between δ¹⁸O SO₄²⁻ and δ¹⁸O H₂O₂; and to apply this relationship to the measured δ¹⁸O H₂O₂, δ¹⁸O SO₄²⁻, and δ¹⁸O H₂O in precipitation water, for assessment of the importance of H₂O₂ in the atmospheric transformation of SO₂ to sulfate.

Development of Analytical Method

No suitable analytical method was available for the quantitative extraction of the oxygen in H₂O₂, (dissolved in water in the ppb range), for isotopic analysis. A 4-step method was developed (4). It consisted

of the removal of dissolved O_2 from 20-liter samples of water by a combination of evacuation, ultrasonic agitation, and sparging with helium; oxidation of the dissolved H_2O_2 to O_2 in the water with $KMnO_4$; removal of the newly formed O_2 from the water in a carrier-gas stream; and conversion of the O_2 to CO_2 by reaction with platinum-catalyzed carbon at $600^\circ C$. The CO_2 was then mass spectrometrically analyzed for its $\delta^{18}O$ (identical to that of the oxygen in the original H_2O_2).

To confirm the absence of appreciable isotopic interference by oxygen exchange between the H_2O and either the H_2O_2 or the O_2 , before, during, or after the oxidation reactions, the reaction was carried out in the presence of three different water supplies of various $\delta^{18}O$. The results in Fig. 1 show that the $\delta^{18}O$ of the CO_2 product was unaffected by the $\delta^{18}O$ of the water solvent.

Synthesis of $\delta^{18}O$ -enriched H_2O_2

Hydrogen peroxides of various $\delta^{18}O$ were not commercially available. A suitable method of synthesis was identified and successfully applied to the laboratory preparations of four stock solutions of H_2O_2 of different $\delta^{18}O$. By this method(5), H_2O_2 is formed by exposure of different supplies of water vapor (each differing in $\delta^{18}O$) to a high-voltage (~ 1.4 kV) discharge in ~ 100 cm of 10-mm o.d. glass tubing between two water-cooled aluminum electrodes. Some of the HO radicals formed by the dissociative reaction



are condensed in a liquid-nitrogen cold trap where they combine to form H_2O_2 , leaving the H radicals to combine in formation of H_2 and be pumped away through the vacuum line.

Other techniques which we experimentally found to give inadequate yields of H_2O_2 were conduction of an electric arc across a stream of aerosolized water droplets (6), excitation of water vapor by a radio-frequency silent discharge in a glass chamber (7.5 cm dia \times 20 cm long) in a commercially available plasma cleaner unit, and excitation by a glow-discharge unit (4.8 cm dia \times 70 cm long) that had uncooled aluminum disk electrodes (7).

Oxidation of SO_2 to SO_4^{2-} by H_2O_2

Using the four stock solutions of hydrogen peroxide, each of different $\delta^{18}O$, sulfate solutions of correspondingly different $\delta^{18}O$ were prepared by oxidation of SO_2 (of constant $\delta^{18}O$) in water ($\delta^{18}O = -7.9\text{‰}$). In Fig. 2 the $\delta^{18}O$ of each resulting sulfate is plotted versus the $\delta^{18}O$ of the H_2O_2 and the equation of the best-fit regression curve is

$$\delta^{18}O_{SO_4^{2-}} = 0.43 \delta^{18}O_{H_2O_2} + 3.5\text{‰} \quad (2)$$

The regression curve of the previously determined (3) relationship between $\delta^{18}O_{SO_4^{2-}}$ and $\delta^{18}O_{H_2O}$ in aqueous-phase oxidation of SO_2 by H_2O_2 was

$$\delta^{18}O_{SO_4^{2-}} = 0.57 \delta^{18}O_{H_2O} - 2.4\text{‰} \quad (3)$$

Assuming that all significant effects of the $\delta^{18}O$ of the SO_2 on the $\delta^{18}O$ of the SO_4^{2-} are lost by rapid isotopic exchange between the SO_2 and the large excess of water, prior to appreciable oxidation (3), $\delta^{18}O_{H_2O}$ and $\delta^{18}O_{H_2O_2}$ remain as the only two complementary variables in the equation for $\delta^{18}O_{SO_4^{2-}}$; therefore, the comprehensive regression curve for $\delta^{18}O_{SO_4^{2-}}$ is

$$\delta^{18}O_{SO_4^{2-}} = 0.57 \delta^{18}O_{H_2O} + 0.43 \delta^{18}O_{H_2O_2} + C \quad (4)$$

$$= \sim \frac{3}{5} \delta^{18}O_{H_2O} + \sim \frac{2}{5} \delta^{18}O_{H_2O_2} + C \quad (5)$$

The constant, C, was evaluated at 8.4‰ from the data given in Fig. 2 by substituting the corresponding measured values for $\delta^{18}\text{O}_{\text{SO}_4^{2-}}$ and $\delta^{18}\text{O}_{\text{H}_2\text{O}_2}$, and -7.9‰ for $\delta^{18}\text{O}_{\text{H}_2\text{O}}$.

The comprehensive equation then became

$$\delta^{18}\text{O}_{\text{SO}_4^{2-}} = 0.57 \delta^{18}\text{O}_{\text{H}_2\text{O}} + 0.43 \delta^{18}\text{O}_{\text{H}_2\text{O}_2} + 8.4\text{‰} \quad (6)$$

and can now be used to calculate $\delta^{18}\text{O}_{\text{SO}_4^{2-}}$ from $\delta^{18}\text{O}_{\text{H}_2\text{O}_2}$ and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ of rainwater for comparison with corresponding measured values of $\delta^{18}\text{O}_{\text{SO}_4^{2-}}$. This comparison may prove to be uniquely useful in the assessment of the importance of H_2O_2 in the oxidation of SO_2 to SO_4^{2-} in the atmosphere.

The slope of 0.43 (approximately 2/5) in Equation 2 of the regression curve through the data of Fig. 2 confirms the evidence of the intermediate species, $\text{H}_2\text{O}_2 \cdot \text{SO}_4^{2-}$, which was previously proposed (3). Apparently, the $\delta^{18}\text{O}$ of the sulfate product is 2/5-controlled by the two oxygens in the H_2O_2 of the adduct, and 3/5-controlled by the SO_4^{2-} , which, in turn, is isotopically controlled by rapid oxygen exchange with the large excess of water with which it is associated.

PRELIMINARY RESULTS

The thrust of this paper is to report the readiness of a new isotopic method for studying the oxidation of SO_2 by H_2O_2 in the atmosphere. So far, the analytical procedure has been applied to samples of rainwater from only two rain events at Argonne, IL. We recognize the uncertainty of the significance of results from so few samples; however, we present them as suggestive of what may follow in more comprehensive sampling programs.

The rainwater was collected by four 1-m² dish-shaped plastic funnels. The funnels were inverted skylights, fitted with drainage connections. Enough water was collected to provide duplicate 20-liter samples from each of the two rains. The first duplicate of each rain was analyzed as soon as operationally practical after collection; the second, a few days later, after storage in the polyethylene bottles in a "cool," unrefrigerated location. The analytical procedure was also applied to a dilute solution of H_2O_2 from a reagent-bottle supply of 30% H_2O_2 (Fisher Scientific Company, H-325 Lot 720017), added to 20 liters of distilled water.

The results of these analyses are given in Table I. The concentrations of H_2O_2 in rainwater (derived from measurement of the CO_2 formed from the O_2 of H_2O_2 origin) ranged from 55 ppb and 35 ppb in the first duplicates of each sample, to 16 ppb and 5 ppb in the second duplicates. The decrease in concentration during storage for each sample was apparently caused by autodecomposition of the H_2O_2 . The $\delta^{18}\text{O}$ of the H_2O_2 (~31‰ for each sample) was relatively high in comparison to that of air oxygen (23.5‰) and very high in comparison to the reagent-bottle H_2O_2 (~-6‰).

The measured values of $\delta^{18}\text{O}$ for sulfate in the first duplicate sample of each rain appeared to be significantly less (2-3‰) than the values calculated from the $\delta^{18}\text{O}$'s of H_2O and H_2O_2 , using Equation 6. This suggests that the SO_4^{2-} in a fresh sample of rain may be a mixture of SO_4^{2-} formed by H_2O_2 oxidation of SO_2 and SO_4^{2-} formed by other mechanisms known to yield lower $\delta^{18}\text{O}$ values (3). The apparent decrease in $\delta^{18}\text{O}_{\text{H}_2\text{O}_2}$ (and correspondingly the calculated $\delta^{18}\text{O}_{\text{SO}_4^{2-}}$) with autodecomposition of the H_2O_2 during storage is surprising and not yet fully understood. Whether the $\delta^{18}\text{O}$ of the residual H_2O_2 increases or decreases during autodecomposition may depend on the catalyst(s) involved in the reaction (8-10).

TABLE I
SUMMARY OF RESULTS, H₂O₂ IN 20-L SAMPLES: REAGENT, RAIN

Sample	Duplicate	Storage		H ₂ O ₂		$\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (measd) (‰)	$\delta^{18}\text{O}_{\text{H}_2\text{O}_2}$ (measd) (‰)	$\delta^{18}\text{O}_{\text{SO}_4^{2-}}$	
		Time (days)	Concentration (ppb)	Recovery (%)	(calcd)* (‰)			(measd) (‰)	
Reagent FSC	1	0	425	95			-5.4		
	2	0	425	96			-6.5		
Rain 9-25/84	1	3	55	-	-4.1	31.1	19.5	16.2	
	2	8	16	-		22.4	15.7		
Rain 10-13-84	1	1	35	-	-3.3	30.8	19.7	17.6	
	2	5	5	-		22.4	16.1		

* $\delta^{18}\text{O}_{\text{SO}_4^{2-}}(\text{calcd}) = 0.57 \delta^{18}\text{O}_{\text{H}_2\text{O}}(\text{measd}) + 0.43 \delta^{18}\text{O}_{\text{H}_2\text{O}_2}(\text{measd}) + 8.4$.

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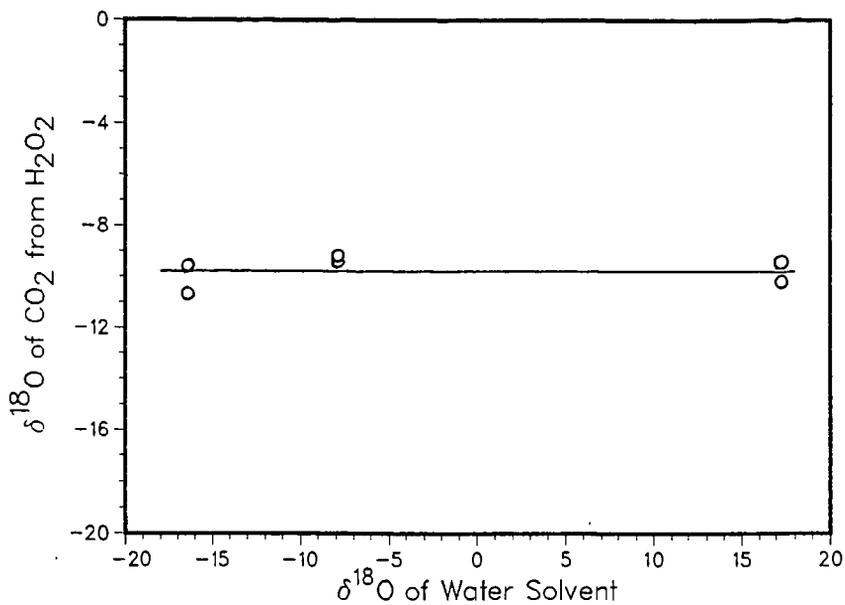


Figure 1. Isotopic influence of water solvent on CO_2 of H_2O_2 origin.

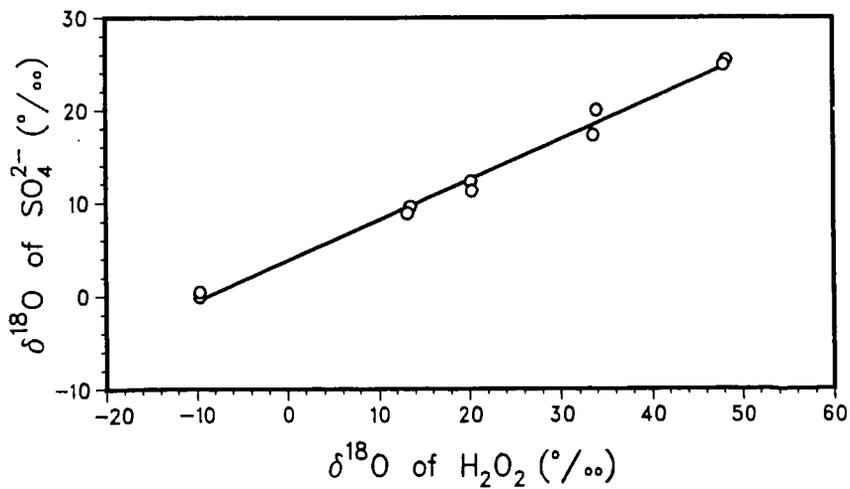


Figure 2. Isotopic influence of the H_2O_2 oxidant on the SO_4^{2-} product.