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MECHANISM OF OXIDATION OF SULFUR DIOXIDE CATALYZED BY PLATINUM

By

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Abstract

It was found that the analysis made by KANEKO and ODANAKA[1,2] with regard to the mechanism of the reaction, $2SO_2+O_2=2SO_3$, catalyzed by platinum was not consistent in their application of the theory of the stoichiometric number[3-5]. Their experimental results were reexamined by considering the forward and the backward unidirectional rates of the oxygen transfers among O_2, SO_2 and SO_3. It was concluded that the sequence of steps, $O_2 \rightleftharpoons 2O(a)$, $SO_2 \rightleftharpoons SO_2(a)$ and $SO_2(a)+O(a) \rightleftharpoons SO_3$, assumed by KANEKO and ODANAKA is effective in a consistent interpretation of their experimental results, however, it results in conclusions that the first one of the above steps is the slowest and the last one nearly in equilibrium, running contrary to the conclusion of KANEKO and ODANAKA that the last step is rate-determining.

§ 1. Introduction

The stoichiometric number, $\nu(r)$, of the rate-determining step, r, of an overall reaction is given by HORIUTI[3] as

$$\nu(r) = -\Delta G/RT \ln(V_+/V_-) \qquad (1)$$

and can be determined by observing the affinity, $-\Delta G$, the steady rate, $V(=V_+-V_-)$, and the forward or the backward unidirectional rate, V_+ or V_-, respectively, of the overall reaction. Practically, V_+ or V_- is evaluated as a transfer rate of an isotope from a reactant to a resultant or the reverse, respectively, in the course of the overall reaction. Accordingly, $\nu(r)$ of Eq. (1) is often found to be infinitely large, as discussed by FRUMKIN[6] and MATSUDA and HORIUTI[4], in the case where the value of V_+/V_- is nearly unity on account of that the isotope used is exchanged through steps nearly equilibrated, other than r. MATSUDA and HORIUTI[4] showed that the determination of a rate-determining step according to the theory of the stoichiometric number[3] was made more reliable by taking account of a set

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of experimental values of $\nu(r)$, inclusive of infinitely large one, which can be obtained by introducing into Eq. (1) the value of V_+/V_- observed by using isotopes of two or more elements involved in the overall reaction.

KANEKO and ODANAKA[1,2] (K.O. in what follows) have applied the theory of the stoichiometric number to the determination of the mechanism of oxidation of sulfur dioxide,

$$2SO_2+O_2=2SO_3, \qquad (2)$$

catalyzed by platinum, using radioactive sulfur and heavy oxygen as isotopic tracers. They have observed the steady oxidation rate, as well as oxygen exchange rate[2] between O_2 labelled by heavy oxygen and normal SO_3, and sulfer oxchange rate[1] between SO_2 labelled by radioactive sulfur and normal SO_3, and found both the values of $\nu(r)$ determined with heavy oxygen and radioactive sulfur to be *ca.* 2. K.O. have thus concluded that step *c* of sequence (3) is the rate-determining one of reaction (2). Their conclusion is adequate only if sequence (3) assumed by them is correct and if V_+ and V_- evaluated by them are the true unidirectional rates of reaction (2).

$$\left.\begin{array}{ll} \text{a}: & O_2 \rightleftharpoons 2O(\text{a}), \\ \text{b}: & SO_2 \rightleftharpoons SO_2(\text{a}), \\ \text{c}: & SO_2(\text{a})+O(\text{a}) \rightleftharpoons SO_3. \end{array}\right\} \qquad (3)$$

The oxygen exchange can, however, take place in the course of reaction (2) not only between O_2 and SO_3 but also between O_2 and SO_2 or SO_2 and SO_3 as observed by K.O. themselves. This fact suggests the evaluation made by K.O. of V_+/V_- to be erroneous. In the present paper the treatment of K.O. and their experimental results are reexamined in the light of a correct application of the theory of stoichiometric number.

§ 2. The results of the treatment of K.O. conflicting with each other.

As mentioned in Introduction, K.O. have determined the stoichiometric number of the rate-determining step of reaction (2) as *ca.* 2 according to Eq. (1) and their experimental results of oxygen exchange between O_2 and SO_3. They have evaluated then V_+/V_- of Eq. (1) according to the equation,

$$V_+/V_- = 1+(z_{O_2}-z_{SO_3})\,\mathrm{d}\,\ln N_{O_2}/\mathrm{d}z_{O_2}, \qquad (4.\text{R})$$

which was derived from the equations for mass balances that

$$V=-\mathrm{d}N_{O_2}/\mathrm{d}t=V_+-V_- \qquad (4.\text{V})$$

and

$$-\mathrm{d}(N_{O_2}z_{O_2})/\mathrm{d}t = z_{O_2}V_+ - z_{SO_3}V_-, \qquad (4.\ z)$$

where N_{O_2} is the number of molecules of O_2 in the reaction system and z_{O_2} or z_{SO_3} the atomic fraction of heavy oxygen, O′, in O_2 or SO_3, respectively. Provided that the above treatment of K.O. is valid, we alternatively have, with regard to the oxygen exchange between SO_2 and SO_3, the equations,

$$V = -\mathrm{d}N_{SO_2}/2\,\mathrm{d}t = V_+ - V_- \qquad (5.\ V)$$

and

$$-\mathrm{d}(N_{SO_2}z_{SO_2})/\mathrm{d}t = 2(z_{SO_2}V_+ - z_{SO_3}V_-), \qquad (5.\ z)$$

which result in

$$V_+/V_- = 1 + (z_{SO_2} - z_{SO_3})\,\mathrm{d}\ \ln N_{SO_2}/\mathrm{d}z_{SO_2}. \qquad (5.\ R)$$

Table 1 shows the experimental results of K.O. Also, in the last two columns are given the values of V_+/V_- evaluated from Eq. (5. R) and those of $\nu(r)$ evaluated by introducing these values of V_+/V_- into Eq. (1). These values of $\nu(r)$ are much larger than 2, and indicate, according to the view of K.O., that the main part of the oxygen exchange between SO_2 and SO_3 is caused by steps other than step *c* of sequence (3). Thus, it is inevitable to introduce a new step of formation of SO_3 besides step *c*, which denies the validity of sequence (3).

TABLE 1. The experimental results of K.O. of oxidation of normal SO_2 by O_2 labelled by heavy oxygen over platinum catalyst and values of V_+/V_- and $\nu(r)$ evaluated according to Eqs. (5 R) and (1), respectively.

Temp. (°C)	Time	P_{O_2} cmHg	P_{SO_2} cmHg	P_{SO_3} cmHg	$z_{O_2}\times10^2$	$z_{SO_2}\times10^2$	$z_{SO_3}\times10^2$	V_+/V_-	$\nu(r)$
395	0 min	12.90	23.34	13.84	9.96	1.40	1.87	1.48	44.5
	33	8.56	14.67	22.50	9.94	1.73	2.63	2.80	14.5
	78	6.40	10.36	26.82	9.94	1.87	2.88	4.67	8.9
	170	4.70	6.96	30.22	9.92	1.95	3.05	8.91	5.6
405	0 hr	8.16	16.87	7.42	11.02	1.64	2.43	1.43	47.7
	1.16	6.71	13.96	10.33	11.00	1.93	2.84	1.75	27.9
	3.75	4.53	9.59	14.70	10.97	2.26	3.35	2.88	13.1
	7.92	1.97	4.49	19.80	10.80	2.52	3.73	7.74	5.3

§ 3. A general consideration of the unidirectional rates of oxygen transfer among O_2, SO_2 and SO_3.

The sequence of steps, (3), excludes *a priori* a chance of oxygen exchange between O_2 and SO_2 without passing through the step of SO_3-formation; such an exchange is called a *direct* exchange in what follows. It is easily seen that direct exchanges of oxygen among O_2, SO_2 and SO_3 are linearly independent of each other, as discussed in Appendix. To investigate the validity of sequence (3), let us start our general consideration from a sequence of steps, which causes an overall reaction,

$$\sum_{i=1}^{3} m_i \mathrm{M}_i = 0, \tag{6}$$

and enables an isotope of an element, A, involved in all of the three species M_i's, to be directly exchanged between any two of them. An example of such a sequence is provided by adding adsorbed sulfur trioxide, $SO_3(a)$, to sequence (3) as

$$\left.\begin{array}{ll} \mathrm{a}: & \mathrm{O_2} \rightleftharpoons 2\mathrm{O(a)}, \\ \mathrm{b}: & \mathrm{SO_2} \rightleftharpoons \mathrm{SO_2(a)}, \\ \mathrm{c}: & \mathrm{SO_2(a)+O(a)} \rightleftharpoons \mathrm{SO_3(a)}, \\ \mathrm{d}: & \mathrm{SO_3(a)} \rightleftharpoons \mathrm{SO_3}. \end{array}\right\} \tag{7}$$

Oxygen exchange between any two of O_2, SO_2 and SO_3 caused by these steps are direct, that is, linearly independent of each other as verified in Appendix. Reaction (6) is a generalized form of the present one, (2), as well as a large number of oxidations, hydrogenations *etc.* of a similar type, and, thus, their mechanisms can be analyzed in the same way as the present treament.

With reference to reaction (6), we now define phenomenologically the forward or backward unidirectional rate, V_{12} or V_{21} respectively, of transfer of A atoms from M_1 to M_2 through the path, M_1-M_2, of direct exchange of A between M_1 and M_2 as follows.

We now denote the isotope of A by A′. V_{12} or V_{13} is the rate of increase of the number of A′ atoms in M_2 or M_3, respectively, and $V_{21}+V_{31}$ that of the number of A atoms in M_1 at the initial stage of reaction (6), where the atomic fractions, z_i's, of A′ atom in M_i's are $z_1=1$ and $z_2=z_3=0$, respectively. V_{21}, V_{23} and $V_{12}+V_{32}$ or V_{31}, V_{32} and $V_{13}+V_{23}$ are defined as the rates similar to those above in a case where $z_2=1$ and $z_1=z_3=0$ or $z_3=1$ and $z_1=z_2=0$, respectively. The unidirectional rates of transfer of A′ atoms from M_1 to M_2, from M_2 to M_1 and so on during reaction (6) of

a mixture of M_1, M_2 and M_3 of z_1, z_2 and z_3, respectively, are now given by z_1V_{12} and z_2V_{21} *etc.* respectively, provided that the isotopic difference between the transfer rates of A and A′ atoms is negligible.

The net rate of reaction (6) is now given as

$$V \equiv dN_i/m_i dt, \tag{8}$$

where N_i is the number of molecules of M_i and dN_i/dt can be expressed in terms of V_{12} *etc.* as

$$dN_1/dt = \frac{1}{n_1}\Big\{(V_{21}+V_{31})-(V_{12}+V_{13})\Big\}, \tag{9.1}$$

$$dN_2/dt = \frac{1}{n_2}\Big\{(V_{12}+V_{32})-(V_{21}+V_{23})\Big\}, \tag{9.2}$$

$$dN_3/dt = \frac{1}{n_3}\Big\{(V_{13}+V_{23})-(V_{31}+V_{32})\Big\}. \tag{9.3}$$

The sign, n_i, in these equations denotes the number of A and A′ atoms in a molecule, M_i, irrespective of their isotopic difference.

With regard to the isotopic exchanges among M_i's, we have

$$n_1 d(N_1z_1)/dt = V_{31}z_3 + V_{21}z_2 - (V_{12}+V_{13})z_1, \tag{10.1}$$

$$n_2 d(N_2z_2)/dt = V_{12}z_1 + V_{32}z_3 - (V_{21}+V_{23})z_2, \tag{10.2}$$

$$n_3 d(N_3z_3)/dt = V_{13}z_2 + V_{23}z_2 - (V_{31}+V_{32})z_3. \tag{10.3}$$

Instead of V_+/V_- in Eq. (1) we derive from Eqs. (9) and (10) the ratios, $R_1 \equiv (V_{12}+V_{13})/(V_{21}+V_{31})$ and $R_2 \equiv (V_{21}+V_{23})/(V_{12}+V_{32})$, as follows. R_1 is the ratio of the unidirectional, transfer rate of the sum total of A and A′ atoms from M_1 to M_2 and M_3 to that of the reverse, and R_2 the ratio defined similarly with regard to M_2.

Dividing the both sides of Eq. (9.1) by $(V_{21}+V_{31})$ we have

$$(V_{12}+V_{13})/(V_{21}+V_{31}) = 1 - n_1(dN_1/dt)/(V_{21}+V_{31}), \tag{11}$$

from which and Eq. (10.1) it follows by elimination of dN_1/dt that

$$n_1N_1dz_1/dt = V_{21}z_2 + V_{31}z_3 - (V_{21}+V_{31})z_1,$$

hence that

$$(V_{21}+V_{31}) = \Big\{n_1N_1dz_1/dt + (z_2-z_3)V_{31}\Big\}\Big/(z_2-z_1) \tag{12.a}$$

or

$$(V_{21}+V_{31}) = \Big\{n_1N_1dz_1/dt + (z_2-z_3)V_{21}\Big\}\Big/(z_3-z_1). \tag{12.b}$$

It follows by substitution of $(V_{21}+V_{31})$ from Eq. (12. a) or (12. b) into Eq. (11)

that

$$R_1 \equiv \frac{(V_{12}+V_{13})}{(V_{21}+V_{31})}$$

$$= 1+n_1(z_1-z_2)(\mathrm{d}N_1/\mathrm{d}t)\Big/\left\{n_1N_1\mathrm{d}z_1/\mathrm{d}t-(z_3-z_2)\,V_{31}\right\} \qquad (13.\ \mathrm{a})$$

or

$$R_1 = 1+n_1(z_1-z_3)(\mathrm{d}N_1/\mathrm{d}t)\Big/\left\{n_1N_1\mathrm{d}z_1/\mathrm{d}t+(z_3-z_2)\,V_{21}\right\}, \qquad (13.\ \mathrm{b})$$

respectively.

Similarly to the above derivation of R_1 it follows from Eqs. (9. 2) and (10. 2) that

$$R_2 \equiv \frac{(V_{21}+V_{23})}{(V_{12}+V_{32})}$$

$$= 1-n_2(z_1-z_2)(\mathrm{d}N_2/\mathrm{d}t)\Big/\left\{n_2N_2\mathrm{d}z_2/\mathrm{d}t+(z_1-z_3)\,V_{32}\right\} \qquad (14.\ \mathrm{a})$$

or

$$\mathrm{R}_2 = 1+n_2(z_2-z_3)(\mathrm{d}N_2/\mathrm{d}t)\Big/\left\{n_2N_2\mathrm{d}z_2/\mathrm{d}t-(z_1-z_3)\,V_{12}\right\}. \qquad (14.\ \mathrm{b})$$

§ 4 Analysis of the experimental results of K.O. according to Eqs. (13) and (14).

We see that the terms in the right-hand side of Eq. (13. a), (13. b), (14. a) or (14. b) are reduced to

$$1+(z_1-z_2)\,\mathrm{d}\ \ln N_1/\mathrm{d}z_1 \equiv R_{1\mathrm{a}}, \qquad (15.\ 1\mathrm{a})$$

$$1+(z_1-z_3)\,\mathrm{d}\ \ln N_1/\mathrm{d}z_1 \equiv R_{1\mathrm{b}}, \qquad (15.\ 1\mathrm{b})$$

$$1-(z_1-z_2)\,\mathrm{d}\ \ln N_2/\mathrm{d}z_2 \equiv R_{2\mathrm{a}}, \qquad (15.\ 2\mathrm{a})$$

or $$1+(z_2-z_3)\,\mathrm{d}\ \ln N_2/\mathrm{d}z_2 \equiv R_{2\mathrm{b}}, \qquad (15.\ 2\mathrm{b})$$

in the paticular case where

$$(z_3-z_2)\,V_{31} = 0, \qquad (16.\ 1\mathrm{a})$$

$$(z_3-z_2)\,V_{21} = 0, \qquad (16.\ 1\mathrm{b})$$

$$(z_1-z_3)\,V_{32} = 0, \qquad (16.\ 2\mathrm{a})$$

or $$(z_1-z_3)\,V_{12} = 0, \qquad (16.\ 2\mathrm{b})$$

respectively. Denoting O_2, SO_2 and SO_3 by M_1, M_2 and M_3, respectively, we find that $R_{1\mathrm{b}}$ and $R_{2\mathrm{b}}$ are just the same as the terms on the right-hand side of Eqs. (4. R) and (5. R), respectively, which have been derived for V_+/V_- by K.O.

We now investigate the magnitudes of R_{1a} *etc.* by comparing them with R_1 and R_2 under the experimental conditions of K.O. With reference to the results of Table 1 we see that

$$z_1 \gg z_3 > z_2 \tag{17}$$

and

$$dN_1/dt,\ dN_2/dt<0 \text{ and } dN_3/dt>0 \tag{18}$$

throughout the course of reaction (2). With reference to these conditions and that V_{12} *etc.* are all positive according to their definitions, we see from Eqs. (13. a), (13. b), (15. 1a) and (15. 1b) that

$$R_{1b} \leqq (V_{12}+V_{13})/(V_{21}+V_{31}) \leqq R_{1a}. \tag{19. 1}$$

It follows similarly from Eqs. (14. a), (14. b), (15. 2a) and (15. 2b) that

$$R_{2b} \leqq (V_{21}+V_{23})/(V_{12}+V_{32}) \leqq R_{2a}. \tag{19. 2}$$

Table 2 shows the values of R_{1a} *etc.* evaluated according to Eqs. (15) from the experimental results at 395°C of Table 1.

TABLE 2. The values of R_{1a}, R_{1b}, R_{2a} and R_{2b} at 395°C evaluated according to Eqs. (15. 1a), (15. 1b), (15. 2a) and (15. 2b), respectively, with reference to the experimental results of Table 1.

Time, min	R_{1a}	R_{1b}	R_{2a}	R_{2b}
0	217.5	205.1	10.1	1.48
33	208.7	185.5	17.3	2.80
78	205.0	179.5	30.5	4.67
170	202.6	174.7	50.2	8.91

We see from Eqs. (19) and the results of Table 2 that $R_1 \equiv (V_{12}+V_{13})/(V_{21}+V_{31})$ is *ca.* 200 practically independent of the progress of reaction (2), whereas $R_2 \equiv (V_{21}+V_{23})/(V_{12}+V_{32})$ is larger than unity, much smaller than R_1 and increases with the progress of the reaction. It follows from Eqs. (8), (9. 1) and (9. 2), where $m_1=1$, $m_2=m_3=2$, $n_1=n_2=2$ and $n_3=3$ in this case, that

$$2\left\{(V_{21}+V_{31})-(V_{12}+V_{13})\right\} = (V_{12}+V_{32})-(V_{21}+V_{23}),$$

which can be reduced to

$$\left\{(V_{21}+V_{23})-(V_{12}+V_{32})\right\}\Big/(V_{12}+V_{13}) \cong 2$$

by neglection of $(V_{21}+V_{31})$ as compared with $(V_{12}+V_{13})$ on account of the value of R_1 much larger than unity. We, thus, have

$$(V_{21}+V_{23})/(V_{12}+V_{13})=2\alpha,$$

where $\alpha>1$.

It follows from this equation and the definitions of R_1 and R_2 that

$$(V_{12}+V_{32})/(V_{12}+V_{13})=2\alpha/R_2 \tag{20. 1}$$

and

$$(V_{21}+V_{23})/(V_{21}+V_{31})=2\alpha R_1 \gg 1. \tag{20. 2}$$

From Eq. (20. 2) we see that

$$V_{23} \gg V_{31},\ V_{21} \tag{21. a}$$

and from Eq. (20. 1) that

$$V_{32} \gtrless V_{13} \tag{21. b}$$

or

$$V_{13} > V_{32},\ V_{12} \tag{21. c}$$

at the early or the later stage of reaction (2), where $2\alpha/R_2 \gtrless 1$ or $2\alpha/R_2<1$, respectively, as seen from the results of Table 2. It is concluded, with reference to the relative magnitudes of V_{12} *etc.* derived above, that the oxygen exchange between SO_2 and SO_3 through the direct path, M_2–M_3, is much faster than those between O_2 and SO_2 through M_1–M_2 and between O_2 and SO_3 by M_1–M_3, hence that these three paths, M_1–M_2 *etc.*, do not include in common the rate-determining step of reaction (2); otherwise the rates of the exchanges through these three paths would not be different from each other.

§ 5 Effectiveness of the sequence of steps, (3).

We see, with regard to the sequence of steps, (3), that the direct path, M_1–M_3 or M_2–M_3, consists of steps *a* and *c* or *b* and *c*, respectively, hence that the conclusion of K.O. that step *c* common to these two paths is rate-determining for reaction (2), conflicts with the present one derived in the foregoing section.

In the foregoing section it has been shown that V_+/V_- evaluated by the treatment of K.O. is identical with R_{1b} or R_{2b} which is the lower bound of R_1 or R_2 respectively and obtained in the case where Eq. (16. 1b) or Eq. (16. 2b) is valid. It must be $V_{12}=V_{21}=0$ in this case on account of $z_1 \neq z_2 \neq z_3$ in the experiments of K.O., that is, the direct oxygen exchange between

O_2 and SO_2 is absent, hence it follows that

$$R_{1b} = V_{13}/V_{31} \quad \text{and} \quad R_{2b} = V_{23}/V_{32} \tag{22}$$

for the sequence of steps, (3).

R_{1b} of Eq. (22) is the ratio of the forward unidirectional rate to that of the reverse of the oxygen transfer through the direct path, M_1–M_3, consisting of steps a and c of sequence (3) and expressed as[5,7]

$$R_{1b} = (v_a/v_{-a})(v_c/v_{-c}), \tag{23. 1}$$

where v_a or v_c is the forward unidirectional rate of step a or c respectively and v_{-a} or v_{-c} is that of the reverse. R_{2b} is similarly given as

$$R_{2b} = (v_b/v_{-b})(v_c/v_{-c}). \tag{23. 2}$$

The ratio, v_s/v_{-s}, of step $s(=a,\ b$ or $c)$ is now recast in the form of[3,4]

$$v_s/v_{-s} = \exp(-\Delta G_s/RT), \quad (s=a,\ b \text{ or } c) \tag{24}$$

where $-\Delta G_s$ is the affinity of step s.

It follows from Eqs. (23), (24) and the values of R_{1b} and R_{2b} given in Table 2, that

$$\Delta G_a/\Delta G_b = \ln(R_{1b}/R_{2b}) = 5.1\sim3.0, \tag{25}$$

which vary with the progress of reaction (2). We have further by substitution of $V_{\ }/V_{\ }$ of Eq. (1) by R_{1b} of Eq. (23. 1) that

$$\nu(r) = -\Delta G/RT\ \ln R_{1b},$$

which can be recast in the form of

$$\nu(r) = \Delta G/(\Delta G_a + \Delta G_c) = \left(\frac{\Delta G_a}{\Delta G_b} + 2 + 2\frac{\Delta G_c}{\Delta G_b}\right)\Big/\left(\frac{\Delta G_a}{\Delta G_b} + \frac{\Delta G_c}{\Delta G_b}\right), \tag{26. ν}$$

by taking Eq. (24) and

$$\Delta G = \sum_s \nu_s \Delta G_s \quad (s=a,\ b \text{ and } c) \tag{26. G}$$

into account, where ν_s is the stoichiometric number of step s and 1, 2 or 2 for step a, b or c, respectively. The value of $\nu(r)$ has been given by K.O. as 2∼2.5 and we see accordingly from Eqs. (25) and (26. ν) that

$$\Delta G_c/\Delta G_b \cong 0. \tag{27}$$

The values of $\nu(r)$ given in Table 1 are easily seen equal to $-\Delta G/RT\ \ln R_{2b}$, which is now recast in the form of

$$\nu(r) = \Delta G/(\Delta G_b + \Delta G_c) = \left(\frac{\Delta G_a}{\Delta G_b} + 2 + 2\frac{\Delta G_c}{\Delta G_b}\right)\Big/\left(1 + \frac{\Delta G_c}{\Delta G_b}\right), \tag{28}$$

similarly to the above derivation of $\nu(r)$. Introducing the values of Eqs. (25) and (27) into above equation, we have

$$\nu(r) = 7.1 \sim 5.0,$$

which is qualitatively in conformity with the result of Table 1, which shows that this value is considerably larger than that evaluated by K.O. according to $\nu(r) = -\Delta G/RT \ln R_{1b}$.

The relative magnitudes of ΔG_a *etc.* given by Eqs. (25) and (27) are consistent, as shown in the followings, with the results of the exchange of radioactive sulfur between SO_2 and SO_3 observed by K.O. in the course of reaction (2).

Provided that this exchange is exclusively caused by sequence (3), we see that only a part of oxygen exchange between SO_2 and SO_3 through the direct path, M_2–M_3, results in the sulfur exchange between them, as exemplified by the following exchanges.

$$S^*OO' + SO_3 \rightleftharpoons S^*O_2 + SO_2O',$$
$$\rightleftharpoons S^*O_2O' + SO_2,$$

where S* denotes an atom of the radioactive sulfur. The second one of the above oxygen exchanges simultaneously results in that of sulfur, but not the first one. Provided that a common fraction, β, of V_{23} and V_{32} contributes to the sulfur exchange between SO_2 and SO_3, we have from Eqs. (9. 2) and (10. 2) with regard to this exchange that

$$n_2 dN_2/dt = V_{32} - V_{23}$$

and

$$n_2 d(N_2 z_2')/dt = \beta z_3' V_{32} - \beta z_2' V_{23},$$

by taking $V_{12} = V_{21} = 0$ into account, where z_2' or z_3' is the mole fraction of radioactive SO_2 or SO_3 respectively. It follows from these equations that

$$V_{23}/V_{32} = 1 + n_2 (dN_2/dt)(z_2' - \beta z_3') \Big/ \left\{ n_2 N_2 dz_2'/dt - (1-\beta) z_2' V_{23} \right\}. \quad (29)$$

In the treatment of K.O. V_-/V_- in Eq. (1) was replaced by V_{23}/V_{32} of Eq. (29), where β was *a priori* treated as unity and $\nu(r)$ was estimated at 2.0∼2.5. Taking $\beta < 1$ and the experimental condition of K.O. that

$$dN_2/dt < 0, \; dz_2'/dt < 0 \quad \text{and} \quad z_2' > z_3'$$

into account, we see that the value of V_-/V_- evaluated by K.O. is the upper bound of V_{23}/V_{32} of Eq. (29). The value of $\nu(r)$ of K.O. is accordingly the lower bound of that correctly evaluated according to Eq. (29) and

$$\nu(r) = -\Delta G/RT \ln(V_{23}/V_{32}). \quad (30)$$

$\nu(r)$ of Eq. (30) is now given by Eq. (28) and evaluated with reference to Eqs. (25) and (27) as 7.1~5.0 in conformity with the above estimation.

Summarizing the above discussions, we see that the sequence of steps, (3), assumed by K.O., is effective in a consistent interpretation of their experimental results, however, it results in a conclusion that the step, $SO_2(a)+O(a) \rightleftharpoons SO_3$, is nearly in equilibrium and the step, $O_2 \rightleftharpoons 2O(a)$, slower than the step, $SO_2 \rightleftharpoons SO_2(a)$, according to the results of the present analysis that $\Delta G_c/\Delta G_b \cong 0$ and $\Delta G_a/\Delta G_b = 5.1 \sim 3.0$.

The present result that the value of $\Delta G_a/\Delta G_b$ varies from 5.1 to 3.0 with the progress of the oxidation of SO_2, is difficult to understand for the present. This variation may be caused by the experimental error of K.O., who have not observed the concentration of SO_2 and the atomic fraction of heavy oxygen in SO_2, but estimated them according to the assumed mass balances of sulfur and respective isotopes of oxygen, or may show the necessity of some improvement of the sequence of steps assumed by K.O. A further detailed discussion of this point is, however, not given for the present.

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Appendix

Discriminating between normal and heavy oxygen atoms, O and O′ respectively, the sequence of steps, (7), in the text is developed into the following eleven steps.

$$\left.\begin{array}{ll} s=1: & O_2 \rightleftarrows 2O\,(a), \\ 2: & OO' \rightleftarrows O\,(a)+O'\,(a), \\ 3: & SO_2 \rightleftarrows SO_2\,(a), \\ 4: & SOO' \rightleftarrows SOO'\,(a), \\ 5: & SO_2\,(a)+O\,(a) \rightleftarrows SO_3\,(a), \\ 6: & SO_2\,(a)+O'\,(a) \rightleftarrows SO_2O'\,(a), \\ 7: & SOO'\,(a)+O\,(a) \rightleftarrows SO_2O'\,(a), \\ 8: & SOO'\,(a)+O'\,(a) \rightleftarrows SOO'_2\,(a), \\ 9: & SO_3\,(a) \rightleftarrows SO_3, \\ 10: & SO_2O'\,(a) \rightleftarrows SO_2O', \\ 11: & SOO'_2\,(a) \rightleftarrows SOO'_2, \end{array}\right\} \qquad \text{(A. 1)}$$

where O'_2, SO'_2 and SO'_3 are neglected to simplify the argument by assuming that the concentration of O' atoms in the reaction system is low enough.

The steady state condition of a reaction consisting of I' intermediates and S steps is given as[4,8],

$$(a_{is})\{v_s\} \equiv 0, \quad (i=1,\ 2,\cdots,I',\ s=1,\ 2,\cdots,S) \qquad \text{(A. 2)}$$

where a_{is} is an element of i-th row and s-th column of matrix (a_{is}) and denotes the number of i-th intermediate formed by a forward act of step s and $\{v_s\}$ a column matrix of the net rate, v_s, of step s. (a_{is}) is now given with regard to the set of steps, (A. 1), as

$$(a_{is}) \equiv \begin{pmatrix} 2 & 1 & 0 & 0 & -1 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & -1 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & -1 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & -1 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & -1 \end{pmatrix}. \qquad \text{(A. 3)}$$

The number, P, of the particular solution of Eq. (A. 2) is that of routes of reaction linearly independent with each other[3,4], and given by $P=S-I$, where I is the rank of matrix (a_{is}) and seven in this case, hence $P=11-7=4$. The four linearly independent routes of reaction are given as

$$\left.\begin{array}{l} \{v_s\}_1 = C_1\{\ 1,\ -1,\ -1,\ 1,\ 0,\ -1,\ \ 1,\ 0,\ 0,\ 0,\ 0\}, \\ \{v_s\}_2 = C_2\{\ 1,\ \ 0,\ \ 2,\ 0,\ 2,\ \ 0,\ \ 0,\ 0,\ 2,\ 0,\ 0\}, \end{array}\right\} \qquad \text{(A. 4)}$$

$$\left.\begin{aligned}\{v_s\}_3 &= C_3\{-1,\quad 2,\quad 2,\ 0,\ 0,\quad 2,\quad 0,\ 0,\ 0,\ 2,\ 0\},\\ \{v_s\}_4 &= C_4\{-3,\quad 4,\quad 2,\ 0,\ 0,\quad 2,\ -2,\ 2,\ 0,\ 0,\ 2\},\end{aligned}\right\}$$

where C_1 *etc.* are arbitrary constants equal to the steady rates of the overall reactions caused by these routes respectively. The four routes linearly independent with each other are not necessarily those of (A. 4) themselves, but also their linear combinations.

The second route of (A. 4) results in the steady oxidation of sulfur dioxide, *i. e.*,

$$2SO_2 + O_2 = 2SO_3. \qquad \text{(A. 5. 1)}$$

The first one of (A. 4) results in

$$O_2 + SOO' = OO' + SO_2. \qquad \text{(A. 5. 2)}$$

By the linear combinations of routes of (A. 4) that

$$\{v_s\}_3 + \{v_s\}_4 \text{ with } C_3 = -C_4 = \frac{1}{2},$$

$$\{v_s\}_1 + \{v_s\}_3 + \{v_s\}_4 \text{ with } C_1 = 1,\ -C_3 = C_4 = \frac{1}{2},$$

and $$\{v_s\}_1 + \{v_s\}_2 + \{v_s\}_3 + \{v_s\}_4 \text{ with } C_1 = C_3 = 1,\ C_2 = C_4 = -\frac{1}{2},$$

it follows as the overall reactions that

$$O_2 + SOO_2' = OO' + SO_2O', \qquad \text{(A. 5. 3)}$$

$$SOO' + SO_2O' = SO_2 + SOO_2' \qquad \text{(A. 5. 4)}$$

and

$$SO_3 + SOO_2' = 2SO_2O' \qquad \text{(A. 5. 5)}$$

respectively. (A. 5. 2), (A. 5. 3) and (A. 5. 4) are the oxygen exchanges between O_2 and SO_2, between O_2 and SO_3 and between SO_2 and SO_3, respectively, and (A. 5. 5) the equilibration of oxygen isotopes among SO_3. Four from these five overall reactions, (A. 5. 1) *etc.*, are linearly independent with each other as mentioned above.

In a case where O_2', SO_2' and SO_3' are taken into account, S and I are 16 and 9 respectively, hence we have seven routes of reaction linearly independent with each other, to which we can apply the equilibration of oxygen isotopes among gaseous oxygen molecules, *i. e.*

$$O_2 + O_2' = 2OO',$$

and that among sulfur dioxide molecules, *i. e.*

$$SO_2 + SO_2' = 2SOO',$$

as well as the five reactions given above. These three equilibrations are not necessary for the present analysis, as it concerns with the atomic fractions of heavy oxygen in oxygen, sulfur dioxide and sulfur trioxide, but not with its detailed distributions among them. We, thus, see that oxygen exchanges between any two of oxygen, sulfur dioxide and sulfur trioxide caused by the sequence of steps, (7), are direct, that is, linearly independent with each other.