

References

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Mechanism for Chemiluminescent Reactions of Bis(2,4,6-trichlorophenyl)oxalate, Hydrogen Peroxide and Fluorescent Aromatic Hydrocarbons

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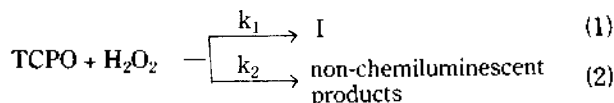
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A mechanistic study on the chemiluminescence resulting from the reaction between bis(2,4,6-trichlorophenyl)oxalate (TCPO) and hydrogen peroxide in the presence of fluorescent polycyclic aromatic hydrocarbons in a viscous phthalate medium has been conducted. The rate determining step, decay rate constants, and relative quantum efficiencies yielded by varying the concentration of reagents generally support an existing mechanism. However, a reaction between TCPO and sodium salicylate was not observed.

Introduction

The chemiluminescence (CL) arising from a reaction of oxalic esters, classified as peroxyoxalate CL, has gained increasing importance for practical CL devices and for utilization to detect fluorescent compounds with a better signal-to-noise ratio than direct excitation using a light source.¹⁻⁵ However, only a limited number of mechanistic studies on the peroxyoxalate CL in a systematic fashion have been performed.^{1,6-8} This is not surprising when one considers the complexities of the chemiluminescent reaction together with the problems associated with a ground-excited state complex for complete description of the reaction. In particular, the identification of the key intermediate and its role responsible for the CL has not been firmly established.⁹

Recently, a detailed quantitative investigation on the base-catalyzed reaction between bis(pentachlorophenyl)oxalate and hydrogen peroxide was conducted and a mechanism modified from existing one was proposed.⁷ If it is applicable to the present system, the rate determining step should be the reaction between TCPO and H₂O₂ and may be represented by



where I stands for a single key intermediate. The key intermediate then reacts and forms a complex with a fluorescer, followed by the emission of light.

Assuming that all the lifetimes of the key intermediate, of a complex between key intermediate and fluorescer, and of the excited state of the fluorescer are short and that their steady-state concentrations are small, the intensity of CL emission at a time t , I_t , should be proportional to the product of TCPO and H₂O₂ concentrations at t ,

$$I_t \propto k_1 [\text{TCPO}] [\text{H}_2\text{O}_2] \quad (3)$$

where k_1 is the second-order rate constant of the reaction(1). However, an experimental evidence of at least two intermediates has been reported for a reaction of TCPO with H₂O₂ and triethylamine.⁸ This possibility was suggested previously.⁹ Therefore, the mechanism awaits further studies.

To elucidate the complex nature of the peroxyoxalate CL, a detailed study has been attempted with TCPO and H₂O₂ using perylene, 9,10-diphenylanthracene (DPA), and rubrene as fluorescers in viscous medium and the results are compared with those of Catherall *et al.*⁷

Experimental

TCPO was prepared by following the method of Mohan and Turro¹⁰ and recrystallized from benzene. H₂O₂ purchased from Riedel-de Haen was vacuum distilled to obtain 94% by weight. Fluorescers, dimethylphthalate, and dibutylphthalate of reagent grade from Aldrich were used without purification, however, tert-butyl alcohol from Junsei was dehydrated with sodium and fractional distilled.

The chemiluminescent reaction was carried out in a 1.0-

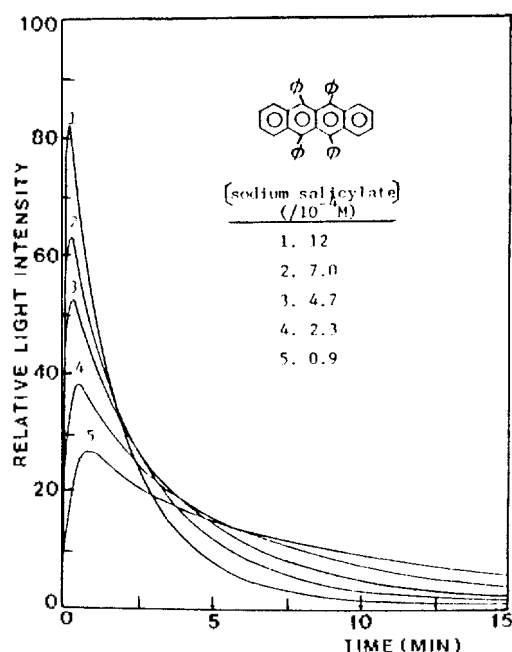


Figure 1. Typical decay of CL intensity for rubrene under the conditions in Table 1.

Table 1. Effect of Sodium Salicylate Concentration (C) on the CL decay Rate Constants (k_d) in units of 10^{-3} sec^{-1} and Relative Quantum Efficiencies (q_r) in an Excess of H_2O_2^a

C $10^{-4}M$	perylene ^b		perylene ^c		DPA		rubrene	
	k_d	q_r	k_d	q_r	k_d	q_r	k_d	q_r
12	—	1.1	9.2	0.11	10.2	0.19	8.2	0.53
7.0	6.3	1.3	6.4	0.15	6.6	0.25	5.7	0.56
4.7	4.5	1.5	4.8	0.19	4.3	0.35	4.4	0.60
2.3	2.0	1.6	2.5	0.29	2.8	0.44	2.9	0.64
0.9	1.5	1.7	1.7	0.40	—	0.63	2.0	0.65
0.7	—	—	1.4	—	—	—	1.5	0.67
0.5	—	—	1.3	—	—	—	1.4	0.68
0.3	1.2	1.7	1.3	0.55	1.5	0.85	1.1	0.69

^aReactant concentration: H_2O_2 , $2.0 \times 10^{-2}M$; TCPO, $5.0 \times 10^{-4}M$; DPA and rubrene, $1.0 \times 10^{-3}M$. ^b $1.0 \times 10^{-3}M$. ^c $5.0 \times 10^{-5}M$.

cm fluorescence cell inserted in a thermostated housing of a Hitachi 650-60 spectrofluorimeter. A 1.5 ml solution of TCPO and a fluorescer in dibutylphthalate was added to the cell. The cell was purged with nitrogen. The reaction was initiated by injecting 0.5 ml solution of H_2O_2 and sodium salicylate in 4:1 dimethylphthalate/*t*-butylalcohol (by volume) purged previously with nitrogen. The decay of CL intensity with time was monitored by the spectrofluorimeter with the lamp turned off at wavelengths such that the reabsorption of emission was negligible. An IBM-4341 computer was used to determine the decay rate constant of the CL intensity and the area under the intensity-time curve.

Results and Discussion

Effect of sodium salicylate. Figure 1 shows typically the concentration dependence of sodium salicylate on the relative CL intensity vs. time in a solution of $5.0 \times 10^{-4}M$

Table 2. Effect of H_2O_2 on the CL Decay rate Constants (k_d) in 10^{-3} sec^{-1} and Relative Quantum Efficiencies (q_r) at Various Excess Concentrations of H_2O_2^a

$\{\text{H}_2\text{O}_2\}_0$ ($/10^{-2}M$)	perylene		DPA		rubrene	
	k_d	q_r	k_d	q_r	k_d	q_r
2.00	3.4	0.24	2.4	0.039	2.8	0.16
1.75	2.9	0.28	2.1	0.042	2.5	0.17
1.50	2.5	0.31	1.7	0.047	2.2	0.17
1.25	2.2	0.33	1.6	0.047	1.8	0.18
1.00	1.8	0.35	1.2	0.052	1.4	0.19
0.75	1.3	0.37	0.9	0.059	1.1	0.20
0.50	0.9	0.39	—	—	0.8	0.21

^aReactant concentration: TCPO; $5.0 \times 10^{-4}M$, sodium salicylate; $1.2 \times 10^{-4}M$, fluorescer; $5.0 \times 10^{-5}M$.

TCPO, $2.0 \times 10^{-2}M$ H_2O_2 , and $1.0 \times 10^{-3}M$ rubrene. The figure revealed that the initial rise up to the maximum intensity was rather rapid while the subsequent decay had an apparent single exponential behavior, indicating that a key intermediate is important. As the concentration of sodium salicylate increased, the time to reach the maximum intensity became slightly shorter and the decay rate turned out to be faster. Table 1 presents quantitatively the effect of sodium salicylate on the CL decay rate constants and relative quantum efficiencies for perylene at two different concentrations, DPA, and rubrene. The relative quantum efficiency is the ratio of the area under the CL intensity-vs.-time curve to the concentration of H_2O_2 .

It is noted from Table 1 that the decay rate constants were essentially independent of the concentration and type of fluorescers, but increased with increasing the concentration of sodium salicylate for all three fluorescers. However, the relative quantum efficiencies showed a reverse trend in comparison with the decay rate constants. These experimental results as to the function of sodium salicylate may be understood in terms of its base catalysis. Increasing the sodium salicylate concentration will enhance the concentration of hydroperoxide, OOH^- , and which will increase the rate of reaction(1) and eventually the rate of CL decay. The enhancement of $[\text{OOH}^-]$ will also promote the nonchemiluminescent path, which results in a decrease of the relative quantum efficiency.

The monotonic increase of the decay rate constants with increasing the sodium salicylate concentration disagrees with the result by Catherall *et al.*,⁷ where the decay rate constants exhibited a maximum. To understand this discrepancy the uv absorption spectra over the region of 200-400 nm were examined. The absorption spectrum of a solution containing both TCPO and sodium salicylate was simply the sum of the spectrum of TCPO and that of sodium salicylate and did not change with time for a period of an hour after mixing the two reagents. The result indicates that no reaction between TCPO and sodium salicylate occurred under the experimental conditions. Thus, the sodium salicylate played a role of mainly enhancing the relative ionization of H_2O_2 instead of forming a more effective base catalyst with TCPO.

Effect of excess H_2O_2 . The data presented in Table 2 summarize the effect of varying H_2O_2 concentration in excess with respect to TCPO on the CL decay rate constants and relative quantum efficiencies when the concentrations of

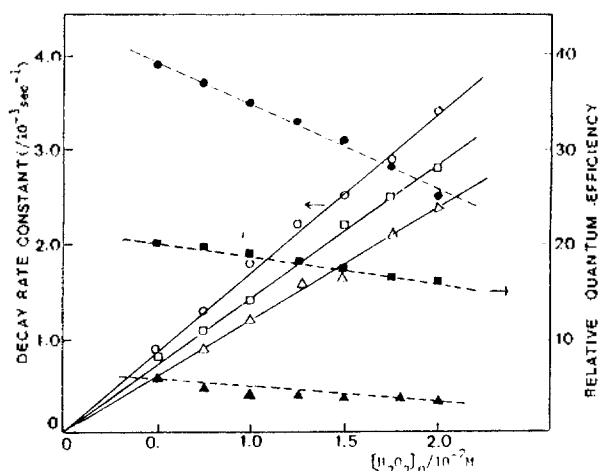


Figure 2. Decay rate constants (perylene(\circ), DPA(Δ), rubrene(\square)) and relative quantum efficiencies (perylene(\bullet), DPA(\blacktriangle), rubrene(\blacksquare)) vs. H_2O_2 concentration under the conditions in Table 2.

Table 3. Effect of the TCPO Concentration on the CL Decay Rate Constants (k_d) in 10^{-3}sec^{-1} and Relative Quantum Efficiencies (q_r) at a Constant Excess Concentration of H_2O_2^a

[TCPO] ₀ (/10 ⁻⁴ M)	perylene		DPA		rubrene	
	k_d	q_r	k_d	q_r	k_d	q_r
2.8	2.59	0.25	1.65	0.06	1.69	0.11
2.4	2.44	0.23	1.53	0.06	1.61	0.11
2.0	2.31	0.25	1.44	0.07	1.51	0.12
1.8	2.24	0.24	—	—	—	—
1.6	2.17	0.27	1.38	0.06	1.42	0.12
1.3	2.06	0.32	1.31	0.07	1.40	0.12
1.1	2.02	0.29	—	—	—	—
0.9	1.92	0.29	1.25	0.07	1.27	0.10

^aReactant concentrations: H_2O_2 ; $2.0 \times 10^{-2}\text{M}$, sodium salicylate; $1.2 \times 10^{-4}\text{M}$, fluorescer; $5.0 \times 10^{-4}\text{M}$.

TCPO, sodium salicylate, and fluorescers were held constant at $5.0 \times 10^{-4}\text{M}$, $1.2 \times 10^{-4}\text{M}$, and $5.0 \times 10^{-5}\text{M}$, respectively. With increasing H_2O_2 concentration the CL decay rate constants showed an increase, but the relative quantum efficiencies decreased. The decline in the latter with increasing $[\text{H}_2\text{O}_2]$ again reflects an increase in the importance of non-chemiluminescent side reactions. The results in Table 2 are plotted in Figure 2 as a function of $[\text{H}_2\text{O}_2]$. The decay rate constants showed a linear relationship, passed through the origin and had a slope of $0.14 \pm 0.03\text{M}^{-1}\text{s}^{-1}$. On consideration of experimental uncertainties, essentially no significant differences in the slopes of three fluorescers were observed, and consequently the fluorescer was not taking part in the rate determining step in agreement with previous work⁷. The disappearance of TCPO by Eqs. (1) and (2) can be written as $-d[\text{TCPO}]/dt = (k_1 + k_2)[\text{TCPO}][\text{H}_2\text{O}_2]$.

Under an excess of H_2O_2 , the concentration of TCPO at t is given by

$$[\text{TCPO}]_t = [\text{TCPO}]_0 \exp \{ - (k_1 + k_2) [\text{H}_2\text{O}_2]_0 t \} \quad (4)$$

where the concentration with subscript "0" implies the initial concentration, and Eq.(3) now becomes

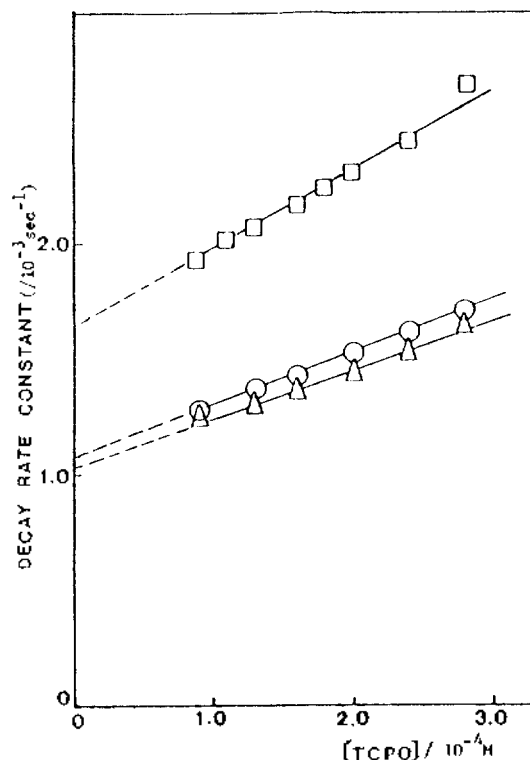


Figure 3. Decay rate constants vs. TCPO concentration for perylene(\square), DPA(Δ), and rubrene(\circ) under the conditions in Table 3.

Table 4. Comparison of Second-order Rate Constants in an Excess of H_2O_2

fluorescer	$k_1 + k_2^a$	slope, $\text{M}^{-1}\text{sec}^{-1}$	intercept, 10^{-3}sec^{-1}	$a[\text{TCPO}]_0 + b$
perylene	0.16	3.40	1.60	0.17
DPA	0.11	2.06	1.05	0.11
rubrene	0.14	2.28	1.10	0.12

^afrom Figure 2.

$$I_t \propto k_1 [\text{TCPO}]_0 [\text{H}_2\text{O}_2]_0 \exp \{ - (k_1 + k_2) [\text{H}_2\text{O}_2]_0 t \} \quad (5)$$

The experimental results agree well with the prediction by Eq.(5) with the decay rate constant being $(k_1 + k_2)[\text{H}_2\text{O}_2]_0$.

Now, the concentration of TCPO in an excess of H_2O_2 was varied to see its function in the CL reaction. Table 3 shows those data for the effect of TCPO concentration on the CL decay rates and relative quantum efficiencies at constant concentrations of sodium salicylate, H_2O_2 , and fluorescers at $1.2 \times 10^{-4}\text{M}$, $2.0 \times 10^{-2}\text{M}$ and $5.0 \times 10^{-4}\text{M}$, respectively. The decay rate constants again showed a linear dependence on the initial TCPO concentration, but had some intercepts as shown in Figure 3, which suggests that the CL intensity with time in an excess of H_2O_2 should follow a relation as

$$I_t \propto \exp \{ - (a[\text{TCPO}]_0 + b) [\text{H}_2\text{O}_2]_0 t \} \quad (6)$$

in conjunction with that of Figure 2. The slope and intercept correspond to $a[\text{H}_2\text{O}_2]$ and $b[\text{H}_2\text{O}_2]$, respectively, from which a and b were calculated using $[\text{H}_2\text{O}_2] = 2.0 \times 10^{-2}\text{M}$.

Since Eqs.(5) and (6) describe the same system in two different ways, $a[\text{TCPO}]_0 + b = k_1 + k_2$. Using the initial TCPO concentrations, a and b , $a[\text{TCPO}]_0 + b$ were computed. The values in the last column of Table 4 are in excellent agree-

Table 5. Effect of H₂O₂ and Fluorescer Concentrations on the CL Decay rate Constants in 10⁻³ sec⁻¹ in an Excess TCPO (4.0 × 10⁻³M)^a

[fluorescer] 10 ⁻⁶ M	[H ₂ O ₂], 4.0 × 10 ⁻⁴ M			[H ₂ O ₂], 2.0 × 10 ⁻⁴ M		
	perylene	DPA	rubrene	perylene	DPA	rubrene
5000	1.7	1.7	1.4	1.6	1.7	1.6
500	1.8	1.5	1.4	1.7	1.5	1.6
50	1.9	1.6	1.5	1.8	1.6	1.6
5	2.1	—	—	1.9	—	—

^aSodium salicylate, 1.2 × 10⁻⁴M.**Table 6. Effect of H₂O₂ Concentration on the CL Decay rate Constants and Relative Total Intensities(Q_T) in an Excess of TCPO (5.0 × 10⁻⁴M)^a**

[H ₂ O ₂] ₀ 10 ⁻⁵ M	rate constant, 10 ⁻⁴ sec ⁻¹			Q _T		
	perylene	DPA	rubrene	perylene	DPA	rubrene
10	2.7	2.2	1.7	6.0	1.8	4.0
5.0	2.6	2.5	1.6	2.9	0.9	1.9
2.5	—	2.1	—	1.2	0.5	0.8

^aSodium salicylate, 1.2 × 10⁻⁴M; fluorescer, 5.0 × 10⁻⁴M.**Table 7. Average Decay rate Constants and Second-order Decay rate Constants in an Excess of TCPO**

TCPO, 10 ⁻⁴ M	(k ₁ + k ₂)[TCPO], 10 ⁻⁴ sec ⁻¹			k ₁ + k ₂ , M ⁻¹ sec ⁻¹		
	perylene	DPA	rubrene	perylene	DPA	rubrene
40	18	16	16	0.45	0.40	0.40
5	2.6	2.3	1.6	0.50	0.44	0.32

ment with $k_1 + k_2$ directly obtained from Figure 2, and are essentially independent of fluorescers.

It may be concluded from the experimental results that under conditions of an excess H₂O₂ the rate determining step of CL emission is the reaction between TCPO and H₂O₂.⁷

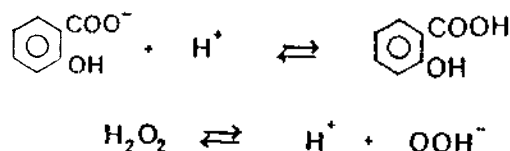
A near constancy of the relative quantum efficiency for each fluorescer in Table 3 is understood as follows. The total number of photons emitted (Q_T) is simply the integral of I, of Eq.(6) with time from $t = 0$ to $t = \infty$, and a calculation of the relative quantum efficiency, $Q_T/[H_2O_2]$, should give a constant, since $a[TCPO]_0 + b$ is a constant. The relative quantum efficiency should, however, be dependent upon the type of fluorescers because of differences in their yields of excitation and fluorescence.

Effect of excess TCPO. When TCPO is in excess over H₂O₂, the CL intensity at any time t is given by a similar equation as Eq.(5), from which H₂O₂ is replaced by TCPO in the exponential term. That is, the CL decay is expected to be independent of H₂O₂ and fluorescers.

The data in Table 5 and 6 agree well with such expectation. Even when fluorescer concentration was varied by a factor of 10³ at two different concentrations of H₂O₂ (Table 5), the decay rate constants remained essentially constant. In another experiment (Table 6), H₂O₂ concentration was varied from 4.0 × 10⁻⁴ M to 2.5 × 10⁻⁵ M and the decay rate constants were fairly unvaried within experimental error.

Also, the relative quantum efficiencies are nearly independent of H₂O₂ as expected. The average of these data are summarized in Table 7 with the second order rate constants, $k_1 + k_2$, obtained from the decay rate constants divided by TCPO concentrations.

When an average value of the second-order rate constants from these two sets of data were computed, $k_1 + k_2 = 0.42 \pm 0.06$ M⁻¹ sec⁻¹ under condition of an excess TCPO. However, the value is approximately three times larger than that obtained in an excess of H₂O₂. This discrepancy in the second-order rate constant seems to arise from the following acid-base equilibria,



The real species to lead a nucleophilic reaction with TCPO is OOH⁻ whose concentration may be assumed constant by the equilibria above under the conditions of an excess H₂O₂. Accordingly, the Eq.(5) should be modified to $I_t \propto \exp\{-(k_1 + k_2)[\text{OOH}^-]t\}$. If the effective concentration of OOH⁻ would be maintained to about 1/3 of the initial H₂O₂ concentration under the condition of excess H₂O₂, two series of measurement would give the same value of $k_1 + k_2$, 0.42. This viewpoint differs somewhat from that by Catherall *et al.*, basically because a reaction between base catalyst and aryl oxalate ester was observed by those authors, but not in the present investigation.

The magnitude of $k_1 + k_2$ is about 40 times smaller than that obtained with bis(pentachlorophenyl)oxalate in chlorobenzene-ethylacetate solvents.⁷ This probably indicates that the chemiluminescent reaction was retarded considerably in a viscous medium ($\eta = 17$ cp) employed here and that the nucleophilic reaction became even slower due to the less electron attracting power of TCPO. A preliminary experiment revealed that the magnitude of $k_1 + k_2$ for perylene obtained in chlorobenzene (90% v/v)-dibutylphthalate solvent ($\eta = 0.9$) was increased by 45% in comparison with that shown above. It appears that the electron attracting power of aryl oxalate plays more important role to the rate constants. More data need to be accumulated to further elucidate the complex nature of peroxyoxalate CL.

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Electrical Conductivity of the System $\text{ThO}_2\text{-Ho}_2\text{O}_3$

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The electrical conductivity of the system $\text{ThO}_2\text{-Ho}_2\text{O}_3$ was measured in the temperature range 600-1100°C and P_{O_2} range $10^{-5.2} \times 10^{-1}$ atm. The mean value of activation energy was 1.45 eV. The observed conductivity dependence on P_{O_2} was $P_{\text{O}_2}^{1/4}$ at P_{O_2} 's above 10^{-3} atm and was independent on oxygen partial pressure at P_{O_2} 's below 10^{-3} atm. It is suggested that these dependences are due to a mixed ionic plus electron hole conduction by V_{O} defect.

Introduction

ThO_2 has the fluorite structure up to its melting point¹, while Ho_2O_3 has the rare earth type cubic structure at temperatures lower than 2200°C. The latter changes to hexagonal in the temperature range 2200 to 2300°C^{2,3}.

ThO_2 was reported to be an n-type semiconductor by Bransky and Tallan⁴ at temperatures above 1600°C and P_{O_2} 's below 10^{-8} atm. This n-typeness was also found by Choudhury and Patterson⁵ at temperatures below 1400°C and P_{O_2} 's lower than 10^{-20} atm. P_{O_2} dependence of the electrical conductivity in pure ThO_2 has also been reported to vary as $P_{\text{O}_2}^{1/5.4}$ and $P_{\text{O}_2}^{1/4.5-8}$ at P_{O_2} 's higher than 10^{-3} atm. In addition to the $P_{\text{O}_2}^{1/5}$ dependence at P_{O_2} 's higher than 10^{-3} atm, Bransky and Tallan⁴ found that the electrical conductivity did not depend on P_{O_2} for P_{O_2} 's between 10^{-8} and 10^{-3} atm.

From the electrical conductivity, mixed ionic and electronic conductivity was observed⁴, and activation energies were reported⁴ to be 0.98 eV and 0.77 eV at temperatures from 700 to 1000°C and above 1000°C, respectively. Bransky and Tallan⁴ reported that the predominant ionic and electronic charge carriers in ThO_2 were fully ionized metal vacancies and electron holes at P_{O_2} 's above 10^{-8} atm. This defect structure was also reported by Bauerle⁸ who attributed his $P_{\text{O}_2}^{1/4}$ dependence to the chemical equilibrium between oxygen gas molecules and fully ionized oxygen vacancies. This defect model and that by Subbarao *et al.*⁹ differ significantly from the fully ionized metal vacancy found by Bransky and Tallan⁴ and from the anti-Frenkel defect *i.e.*, O_i in pure ThO_2 observed by Lasker and Rapp.⁶ Hardaway *et al.*¹⁰ reported the maximum electrical conductivity in ThO_2 doped with 7.5 mol % Y_2O_3 (15 mol % $\text{YO}_{1.5}$) which has already been observed by Lasker and Rapp⁶.

In this work $\text{ThO}_2\text{-Ho}_2\text{O}_3$ systems were prepared, and their electrical conductivities were measured as a function of temperature and P_{O_2} . From the temperature and P_{O_2} dependences of electrical conductivity, one defect model and two carrier types are proposed.

Experimental

Sample preparation. ThO_2 and Ho_2O_3 powders obtained both from the Johnson-Matthey Co. (99.99%) were separately calcinated at 800°C for 6 hr; then weighed, mixed in varying proportions, ballmilled for several hours in $\text{C}_2\text{H}_5\text{OH}$ solution and then dried at 300°C. The powder mixtures were compacted into pellets under a pressure of 48 MPa in vacuum. Pellets of ThO_2 containing 5, 8, 10, 12 mol % Ho_2O_3 were sintered for 48 hr at 1400°C, annealed for 72 hr at the same temperature under atmospheric pressure, and then quenched to room temperature. The pellets were given a light abrasive polish on both faces until voids on the faces were fully eliminated. The specimens were cut into rectangular forms having dimensions of approximately $1.5 \times 0.7 \times 0.4 \text{ cm}^3$. Four holes were drilled into the largest face at intervals of 0.2 cm. The specimens were etched in dilute HNO_3 solution, washed with distilled water, and dried in an oven at 200°C for about 24 hr. As Keller *et al.*¹¹ and Sibieude and Foex¹² reported, X-ray analysis confirmed that all sintered specimens had ThO_2 type solid solution. Pycnometric densities of specimens are more than 96% of theoretical densities. Spectroscopic analysis of the specimens above showed that total amount of impurity was lower than 20 ppm. Before the sample was introduced into the sample basket, it was always etched in $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and dilute HNO_3 , and washed with distilled water, dried, and then connected to the Pt probes.

P_{O_2} establishment. The various oxygen partial pressures were established using pure oxygen or nitrogen or a mixture of 0.001% oxygen in nitrogen obtained from Matheson Gas Products. The quartz sample basket was evacuated to a pressure of 1×10^{-7} torr by a diffusion pump¹³ at room temperature, and then the temperature of the sample container was increased up to 200°C. A mixture of oxygen and nitrogen, or pure oxygen, was introduced into the sample basket, which was then evacuated again to a pressure of 1×10^{-6}