

the aromatic ring leading to a halonium ion<sup>10b</sup>; halogenation led to monohalogenated resorcinols. The suggested ready formation of a positive halogen species should make possible the introduction of various new synthetic methodologies.

In summary we have described a new halogenation reagent which is easy to handle and which has certain advantages over the existing ones used in halogenation of resorcinols and bromination of monoethyl resorcinol, in particular as regards monohalogenation, regioselectivity and, in most cases, yields.

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## Purification of $TiCl_4$ by Adsorption Technique

Q. Won Choi\*, and Kyung Ae Lee

Department of Chemistry, College of Nature Sciences, Seoul National University, Seoul 151

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Titanium tetrachloride is purified using adsorption column packed with activated silica gel. When 120 ml of titanium tetrachloride was passed through an adsorption column filled with 7 g silica gel, iron content in titanium tetrachloride has been reduced from 7 ppm to less than 1 ppm, and aluminum from 46 ppm to 11 ppm, while silicon content being unchanged at about 60 ppm.

### Introduction

Various methods currently in use for the preparation of high-purity titanium dioxide require titanium tetrachloride as a source material. The quality of titanium dioxide depends on the purity of the titanium tetrachloride used. Titanium tetrachloride is highly volatile; consequently, distillation may serve as a reasonably effective and convenient method of removing nonvolatile impurities<sup>1-3</sup>. However, it is difficult to remove low level volatile impurities such as iron (III), aluminum, silicon chlorides, etc.

It has been reported that ferric chloride, as well as heavy metal chlorides are removed from silicon tetrachloride efficiently by adsorption on silica gel<sup>4</sup>.

In the present study, an attempt has been made to purify titanium tetrachloride by passing titanium tetrachloride through column packed with activated silica gel.

### Experimental

#### Purification of $TiCl_4$ by the adsorption method

Since the titanium tetrachloride is very sensitive to moisture, the experiment was performed in a glove box under flowing dry  $N_2$  gas. Some silica gel was also placed in the glove box. A blower was used inside the glove box for forced air convection. The separation column was constructed so that  $TiCl_4$  was kept in a closed system during the separation as shown on Figure 1.

As the adsorbent, purified silica gel<sup>5</sup> of 70-230 mesh was used; it was activated by heating in air at  $270 \pm 10^\circ C$  for 18 hours prior to use<sup>6</sup>. About 7 g of the activated silica gel was packed a portion of the adsorption column about 25 cm long.  $TiCl_4$  was allowed to drop on top of the adsorbent at a rate of about  $1 \text{ ml min}^{-1}$  while suction was applied, until a liquid column was formed in the delivery tube. After standing for 30 minutes,  $TiCl_4$  was allowed to flow while draining at a rate of  $0.1 \text{ ml min}^{-1}$ . After flowing every 40 ml, about 2 ml of the eluent was collected in a vessel containing 20 ml of distilled 6M HCl for chemical analysis.

After passing about 150 ml of  $TiCl_4$ , the silica gel in the top 6 cm portion of packing was transferred to 50 ml beaker with 6M HCl. The remainder was transferred to 100 ml

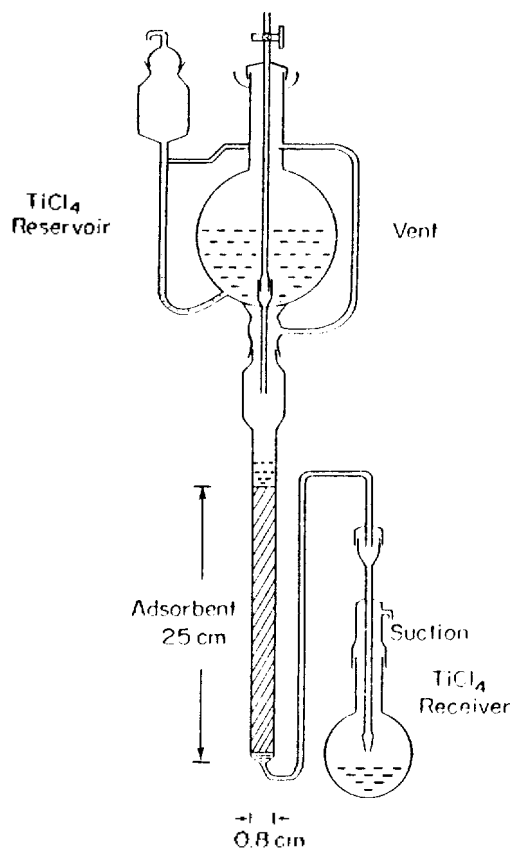


Figure 1. Adsorption apparatus for the purification of  $\text{TiCl}_4$ .

beaker. Silica gel was separated by decantation and washed twice with HCl after allowing to stand 2 days. The solutions were analyzed by the procedure given below.

Iron remaining in the silica gel was determined after treating the dried sample with HF and  $\text{H}_2\text{SO}_4$ .

#### Determination of Fe, Al and Si

##### A) Determination of Iron in $\text{TiCl}_4$ by Ferrozine

All glass wares were cleaned and soaked in conc. HCl for 5 hours. All solutions used in this study were prepared with doubly distilled water.

To the solution containing 0.1-0.2g of  $\text{TiCl}_4$  in 2.5 M HCl 1 ml of acid reagent solution prepared from ferrozine and hydroxylamine hydrochloride in HCl, and 1 ml of tartaric acid (20% solution) was added. The pH of the solution was adjusted to 5.5 by ammonium acetate and ammonium hydroxide buffer solution and the absorbance was measured at 561 nm<sup>7</sup>.

##### B) Determination of Al in $\text{TiCl}_4$

The direct application of the colorimetric determination of aluminum in titanium tetrachloride without separating the major portion of titanium was not possible because of the marked interference. Thus, titanium was precipitated by cupferron<sup>8,9</sup>. In addition to removing titanium, the cupferron precipitation also serves to remove iron which would also interfere. After removing titanium by cupferron, aluminum quinolate has been quantitatively extracted with chloroform at pH = 9. The absorbance was measured at 390 nm<sup>10</sup>.

##### C) Determination of Silicon in $\text{TiCl}_4$ <sup>11-13</sup>

Titanium in  $\text{TiCl}_4$  solution was precipitated by hydrolysis. Ammonium molybdate was added to form the yellow silico-

Table 1. The Contents of Fe, Al and Si in  $\text{TiCl}_4$  before and after Passing Silica gel Column

impurity	before purification (ppm)	after purification (ppm)
Fe	7	<1
Al	46	11
Si	60	61

Table 2. The Contents of Fe in HCl Washings of Silica gel and in Silica gel Residue used after the Elution of  $\text{TiCl}_4$

washings of silica gel		residue of silica gel		total Fe
dark brown portion	residual portion	dark brown portion	residual portion	
0.23mg	0.02mg	0.6mg	0.2mg	1.05mg

molybdate color, then added tartaric acid to stabilize this color and mixture of 1-amino-2-naphthol-4-sulfonic acid, sodium sulfite and sodium bisulfite as the reducing agent. The molybdenum blue color was developed in the presence of the Ti-hydroxide precipitate. After filtration, the absorbance at 700 nm was measured<sup>11</sup>.

## Results and Discussion

It was observed that after several milliliters of  $\text{TiCl}_4$  have been passed, a band of brown coloration appeared at the top of the column. This band gradually broadened with continued use. After flowing of 40 ml  $\text{TiCl}_4$ , brown band was extended down forming 2 cm of dark brown and 6 cm of pale brown portions. After flowing 120 ml, the dark brown band was extended to 5 cm and the pale brown band to 21 cm. After flowing 150 ml  $\text{TiCl}_4$ , the pale brown color was extended down to the lower end portion of the silica gel.

The samples of eluent  $\text{TiCl}_4$  obtained after flowing every 40 ml were analyzed. Table 1 is the analytical data for Fe, Al and Si before and after passing the silica gel column. Iron was not detected (<1 ppm) until 120 ml of  $\text{TiCl}_4$  was collected, whereas the concentration of iron in the  $\text{TiCl}_4$  became noticeable at 4 ppm when the amount of eluted  $\text{TiCl}_4$  exceeded about 150 ml.

The washings and washed silica gel were analyzed for iron. Table 2 gives the result of analysis for iron. The total amount of Fe recorded by chemical analysis of silica gel packing after use is 1.05 mg which is smaller than the amount of Fe (about 1.2 mg) expected to be removed from about 120 ml of  $\text{TiCl}_4$  (1.7 Kg  $\text{l}^{-1}$ ) of 6 ppm. The difference may be due to the errors from the weighing of  $\text{TiCl}_4$  which is very sensitive to moisture, and from the volume measurement of the eluent measured by the flask which has marker scale.

Thus, it can be concluded that about 120 ml of  $\text{TiCl}_4$  can be purified by using 7 g of activated silica gel. Although Fe and Al can be removed from  $\text{TiCl}_4$  solution, Si cannot be removed by adsorption by activated silica gel.

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

Hyung-Soo Song, Hyung Seon Shin, and Kang-Jin Kim\*

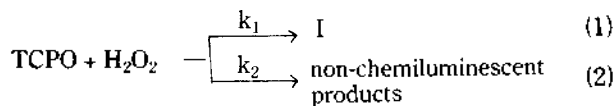
Department of Chemistry, Korea University, Seoul 136. Received September 1, 1987

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.<sup>1,5</sup> However, only a limited number of mechanistic studies on the peroxyoxalate CL in a systematic fashion have been performed.<sup>1,6,8</sup> 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.<sup>9</sup>

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.<sup>7</sup> If it is applicable to the present system, the rate determining step should be the reaction between TCPO and H<sub>2</sub>O<sub>2</sub> 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 H<sub>2</sub>O<sub>2</sub> 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 H<sub>2</sub>O<sub>2</sub> and triethylamine.<sup>8</sup> This possibility was suggested previously.<sup>9</sup> Therefore, the mechanism awaits further studies.

To elucidate the complex nature of the peroxyoxalate CL, a detailed study has been attempted with TCPO and H<sub>2</sub>O<sub>2</sub> using perylene, 9,10-diphenylanthracene (DPA), and rubrene as fluorescers in viscous medium and the results are compared with those of Catherall *et al.*<sup>7</sup>

### Experimental

TCPO was prepared by following the method of Mohan and Turro<sup>10</sup> and recrystallized from benzene. H<sub>2</sub>O<sub>2</sub> 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-