

THE THERMAL DECOMPOSITION OF PLATINUM(II) AND (IV) COMPLEXES

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ABSTRACT

The decomposition characteristics of Pt(II) and Pt(IV) complexes in hydrogen, air and argon were investigated by thermal gravimetric and differential thermal analysis. Based on weight-loss measurements, the thermal stability in hydrogen increased in the order: hexachloroplatinic acid < platinum acetyl acetonate < platinum diamino dinitrite < tetrammine platinous hydroxide < tetrammine platinous chloride < platinum phthalocyanine; whereas in air, the order was: hexachloroplatinic acid < tetrammine platinous hydroxide < platinum acetyl acetonate < platinum diamino dinitrite < tetrammine platinous chloride. The platinum complexes were more stable in air than in hydrogen where decomposition was observed in all platinum samples at temperatures below 200°C.

INTRODUCTION

Platinum is commonly used as a catalyst for many gas-phase and liquid-phase reactions. To increase the catalyst surface accessible to the reactant species the platinum is dispersed on a high surface area porous support (silica, alumina, carbon, etc.). Two techniques commonly employed to obtain high surface area supported platinum catalysts are the so-called ion-exchange and impregnation methods¹⁻⁵. The former technique involves the exchange of a platinum cation, usually $\text{Pt}(\text{NH}_3)_4^{2+}$, for protons on the surface of the support whereas the latter involves evaporating to dryness a platinum salt solution impregnated in the porous support. One of the final steps in catalyst preparation is the decomposition of the ion-exchanged platinum cation or the impregnated platinum salt. However, the temperatures at which the decomposition step is conducted and the gaseous environment generally employed to optimize the platinum dispersion have not been systematically investigated.

The purpose of the present paper is to determine by thermal gravimetry (TG) and differential thermal analysis (DTA) the decomposition characteristics of platinum salts commonly employed in supported catalyst preparation. To the authors knowledge, very little has been published on the thermal stability of the platinum com-

pounds, platinum diamino dinitrite, tetrammine platinous chloride and hexachloroplatinic acid in the gaseous environments used in the present study, namely hydrogen, argon and air. In addition, platinum acetyl acetonate, tetrammine platinous hydroxide and platinum phthalocyanine were examined by TG to determine the influence of various ligand groups on the thermal stability of platinum complexes.

Although TG is a well-established technique, its use in catalyst studies has been rather limited. Newkirk and McKee⁶ employed TG to determine the decomposition temperatures of rhodium, iridium and ruthenium chlorides in hydrogen and air, and also investigated the influence of catalyst supports on the reduction temperatures of these noble metal salts. Thermal analysis techniques were also employed by Morikawa et al.⁴ to study the formation of nickel aluminate during the preparation of supported nickel on alumina catalysts.

EXPERIMENTAL

Apparatus

A glass chamber containing a Cahn microbalance (Model 2000 RG) was connected to a quartz hang-down tube (41 mm O.D.) approximately 100 cm long. This allowed a separation of 60 cm between the tube furnace surrounding the sample and the delicate balance mechanism. The gases used in the present study were first passed through flow meters, then into the glass chamber and down the hang-down tube. This prevented any corrosive decomposition gases formed in the hot zone from reaching the balance. After passing through the sample zone, the gases were vented out of the bottom of the hang-down tube. A 20-mil diameter quartz fiber was used to connect the microbalance to the quartz sample holder (hemispherical, 1 cm diameter). The quartz fiber and sample holder had a total weight of less than 200 mg and the sample weights were in the range 10–50 mg. Combination of these weights allowed operation of the microbalance with a weight change of 1 mg recorded as the full scale reading on a 10-in. strip chart recorder.

A chromel-alumel thermocouple was placed adjacent to the outside of the hang-down tube enclosed by the heater. This thermocouple was connected to a temperature controller (designed in this laboratory) which programmed the linear heating rate applied to the sample. The temperature of the sample was taken to be the same as that monitored by the thermocouple placed 1 cm below the sample holder and in the center of the hot zone. In general, a sample heating rate of 10 ± 1 °C min⁻¹ was used and the gas flow-rate was 100 cm³ min⁻¹ at room temperature (22 °C) and atmospheric pressure.

Preliminary experiments were performed to determine the buoyancy correction to the sample weight due to thermal convection and gas flow through the hang-down tube. Using a 20-mg Pt metal test sample, the maximum deviation from the initial sample weight was ± 0.03 mg at temperatures below 450 °C. Hence, under these conditions no correction was applied for apparent weight changes during a thermal experiment.

The DTA data were obtained on a Netzsch automatic recording system. The sample (30–170 mg) was placed in a small alumina container constructed with a central concave area which was positioned over a Pt/Pt-10 Rh thermocouple. A reference standard kaolin was used which was packed in a similar alumina container and positioned 1 cm from the sample. The differential potential output measured between thermocouples positioned below the sample and the standard was recorded on a strip chart recorder. The furnace surrounding the sample and standard was programmed for a heating rate of $10^{\circ}\text{C min}^{-1}$. Gases used in the TG experiments were also used in the DTA experiments, however, the gas flow-rate over the sample could not be easily controlled. The gas was vented out of the DTA apparatus through a small constriction and for all practical purposes, the gas in the DTA cell can be considered as stagnant. Therefore, the experimental conditions are not similar to those used in the TG studies and any interpretations of the DTA results will be of a qualitative nature.

Chemicals

Five platinum compounds were examined without further purification. Tetramine platinumous chloride $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot 0.3\text{H}_2\text{O}]^*$ and platinum acetyl acetonate $[\text{Pt}(\text{C}_5\text{H}_7\text{O}_2)_2]$ with Pt content** of 57.50 and 49.73 wt.%, respectively, were obtained from Matthey Bishop Inc. (Malvern, Pa). Platinum diamino dinitrite $[\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2]$ and hexachloroplatinic acid $[\text{H}_2\text{PtCl}_6 \cdot 4.4\text{H}_2\text{O}]^*$ with Pt content** of 61 and 40 wt.%, respectively, were obtained from Engelhard Ind. (Newark, N.J.). Finally, platinum phthalocyanine $[\text{C}_{32}\text{H}_{16}\text{N}_8\text{Pt}]$ obtained from K & K Laboratories (Plainview, N.Y.) had a Pt content of 16 wt.% determined by atomic adsorption.

A sample of $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$ was prepared by passing a solution of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ through the hydroxyl form of an ion-exchange resin (Amberlite RA-400, Rohm and Haas Co.) column¹. Analysis of the resulting solution showed only $22 \mu\text{g Cl}^- \text{ ml}^{-1}$ were present (initially $2 \text{ mg Cl}^- \text{ ml}^{-1}$ in the $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ solution) which suggested the hydroxyl form of the platinum ammine complex was formed. The $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$ solution was evaporated to dryness in a vacuum desiccator and the white precipitate was used without further purification.

The gases (air, Ar, H_2O , O_2) were of commercial grade ($\geq 99\%$ purity) and used without further purification.

DISCUSSION OF RESULTS

Thermal gravimetry

Although the thermal decomposition of chloroplatinic acid was investigated many years ago⁷, it was felt that this platinum compound would serve as a useful starting point for testing our thermal analysis techniques and allow comparison of its

*Moles H_2O calculated from Pt content in complex.

**Values quoted by the manufacturer.

thermal stability with other platinum salts under comparable conditions. The thermal decomposition of $\text{H}_2\text{PtCl}_6 \cdot 4.4\text{H}_2\text{O}$ in various gaseous environments is plotted in Fig. 1. The results obtained in argon, air and oxygen were all similar (Fig. 1, curve B),

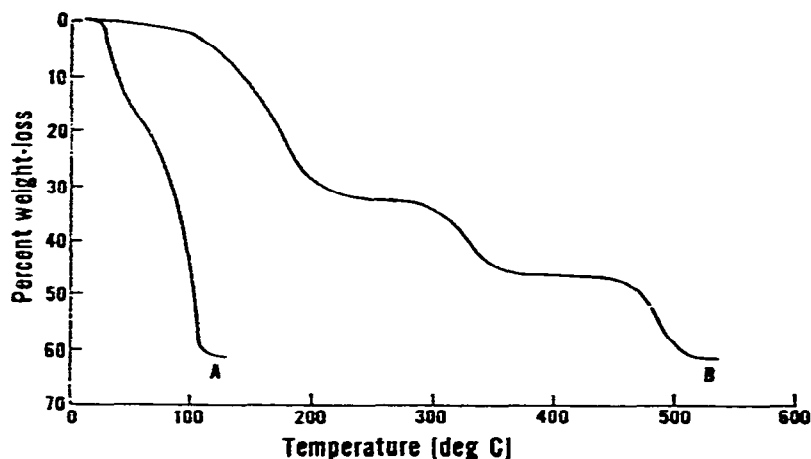


Fig. 1. TG of chloroplatinic acid in hydrogen (A) and air (B).

indicating the presence of two distinct compounds. Based on the weight-loss (33%), the first dissociation step can be represented by the reaction



The theoretical weight-loss for this reaction (31%) is in good agreement with the measured value obtained in argon, oxygen and air. The weight-loss for the second dissociation step (14%) corresponds to the loss of two chlorine atoms (14.5%). The last dissociation step involves the same weight-loss as the second and must therefore represent the loss of the remaining chlorine, leaving metallic platinum as the solid residue. According to Gmelin⁷, heating in a dry air stream at 200°C for 4½ h resulted in a mixture of 94% PtCl_4 and 6% PtCl_2 , in qualitative agreement with our weight-loss measurements. When the thermal decomposition is carried out in flowing hydrogen, $\text{H}_2\text{PtCl}_6 \cdot 4.4\text{H}_2\text{O}$ decomposes at a considerably lower temperature (Fig. 1) with no distinct intermediate products being formed.

The thermal decomposition of $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ occurred with a rapid weight-loss at well-defined temperatures. An example of the rapid weight-loss monitored on the strip chart recorder for thermal decomposition in flowing hydrogen is shown in Fig. 2. $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ samples did not show any appreciable change in weight until the decomposition temperature was reached, then the decomposition reaction was so violent that some of the platinum salt was spewed out of the sample holder. Similar rapid changes in $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ sample weight occurred in argon, air and oxygen. It is evident that the decomposition temperature is very dependent on the surrounding gas environment (see Table 1) and furthermore, even in a vacuum produced with a mechanical pump, $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ undergoes violent decomposition at a lower

temperature than in air or argon. According to Figueras et al.⁸, the ligands in $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ decomposed in a vacuum into nitrogen and water.

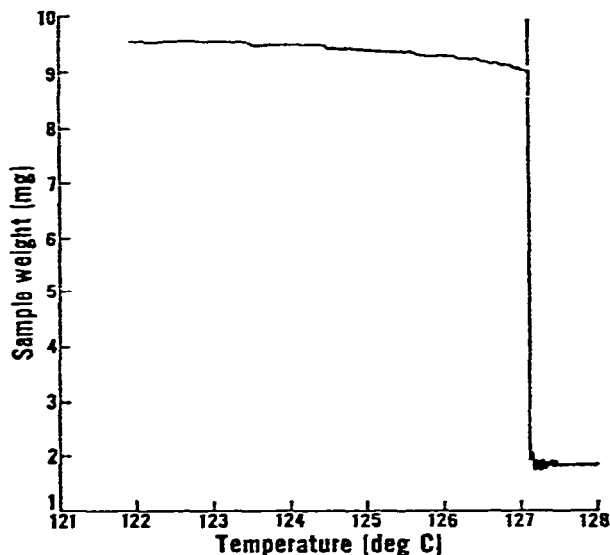


Fig. 2. Weight-loss measurement of platinum diamino dinitrite during rapid thermal decomposition in hydrogen.

TABLE I

THERMAL DECOMPOSITION TEMPERATURES OF $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ IN A FLOWING GAS STREAM

<i>Gas environment</i>	<i>Decomposition temperature (°C)</i>
Hydrogen	127
Argon	208
Air	230
Oxygen	232
Vacuum	180

TG of Pt(II) compounds in flowing air yielded the thermograms plotted in Fig. 3. The impure $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$ sample underwent thermal decomposition at a lower temperature than $\text{Pt}(\text{C}_5\text{H}_7\text{O}_2)_2$ or $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot 0.3\text{H}_2\text{O}$. The weight-loss of 40%, obtained with $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$, is larger than the calculated value (34.4%) for the decomposition of the pure sample to platinum metal. This discrepancy reflects the presence of a chloride impurity in the sample, resulting from the ion-exchange step. The thermograms of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot 0.3\text{H}_2\text{O}$ obtained in air and argon were the same, showing evidence for an intermediate product in the weight-loss curve. In the temperature range 180–260°C, Wendlandt⁹ observed in air the evolution of NH_3 from the anhydrous compound, $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$, to form the diammine salt *trans*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$.

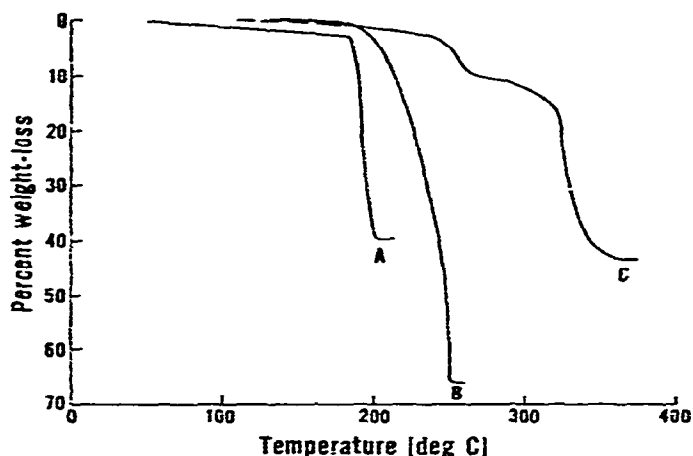


Fig. 3. TG of platinum salts in air. (A) tetrammine platinous hydroxide; (B) platinum acetyl acetonate; (C) tetrammine platinous chloride.

Then, at approximately 320°C, decomposition to metallic platinum was observed. Block et al.¹⁰ also reported that $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ decomposed in air accompanied by the evolution of NH_3 , however, they reported a lower decomposition temperature (220–250°C) for *trans*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ than observed by Wendlandt. The thermogram for $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$ shown in Fig. 3 is in qualitative agreement with the reported results of Wendlandt⁹ and Block et al.¹⁰. The acetyl acetonate derivative of various metals have been observed to sublime upon heating in air¹¹ and platinum acetyl acetonate was no exception. After thermal decomposition of $\text{Pt}(\text{C}_5\text{H}_7\text{O}_2)_2$ had taken place in air, the sample holder and the hang-down tube were coated with a platinum film. Furthermore, the weight-loss measured was considerably greater than the calculated value for platinum acetyl acetonate, suggesting the loss of platinum from the sample holder.

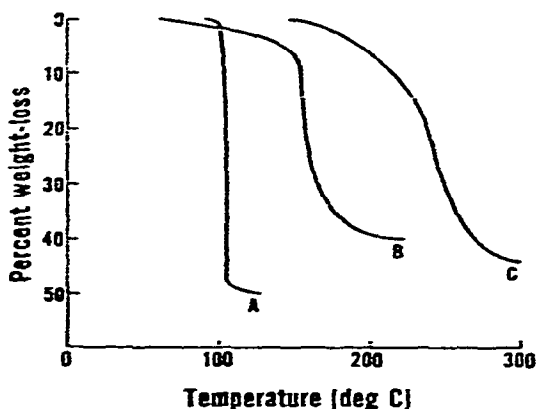


Fig. 4. TG of platinum salts in hydrogen. (A) platinum acetyl acetonate; (B) tetrammine platinous hydroxide; (C) tetrammine platinous chloride.

When the same platinum compounds decomposed in air were examined in hydrogen, the thermograms recorded in Fig. 4 were obtained. In each case, thermal decomposition of the platinum compound occurred at a lower temperature in hydrogen than in air. The reduction of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot 0.3\text{H}_2\text{O}$ in hydrogen showed no inflection in the thermogram (Fig. 4) which suggested that the decomposition must involve a single-step process. The measured weight-loss of 44% is in good agreement with the calculated value (42.5%) for decomposition to metallic platinum. Similarly, the lack of any inflections in the thermograms for $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$ suggested dissociation occurred in a single-step process. Whereas sublimation of platinum acetyl acetonate occurred while heating in air, decomposition in hydrogen resulted in the reduction to platinum metal. The measured weight-loss of 50% agreed very well with the calculated value (50.27%) for $\text{Pt}(\text{C}_5\text{H}_7\text{O}_2)_2$.

All the platinum compounds examined above by TG started to decompose at a temperature lower than 200°C in flowing hydrogen. In view of the high thermal stability reported for phthalocyanines^{12,13}, the thermal decomposition of platinum phthalocyanine was examined in flowing hydrogen for comparison with the above-mentioned platinum compounds. The thermogram shown in Fig. 5 indicated that a weight-loss was measured at approximately 200°C , however, even at 800°C , decomposition to platinum metal was not complete and a weight-loss was still observed. Barrett et al.¹³ reported that platinum phthalocyanine sublimed at about 550°C , however, there was no direct evidence in the present study to suggest this occurred in flowing hydrogen.

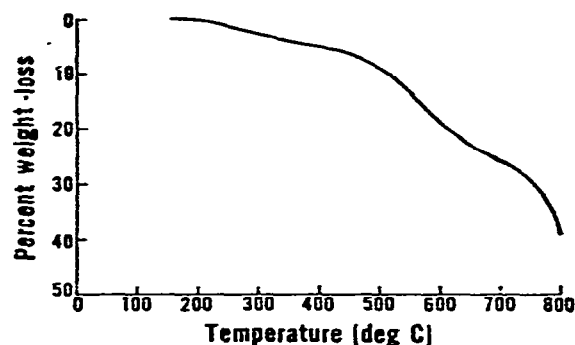


Fig. 5. TG of platinum phthalocyanine in hydrogen.

The thermal stability of the platinum compounds investigated in the present paper can be ranked, based on weight-loss measurements. In hydrogen, thermal stability increased in the order: $\text{H}_2\text{PtCl}_6 \cdot 4.4\text{H}_2\text{O} < \text{Pt}(\text{C}_5\text{H}_7\text{O}_2)_2 < \text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2 < \text{Pt}(\text{NH}_3)_4(\text{OH})_2 < \text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot 0.3\text{H}_2\text{O} < \text{C}_{32}\text{H}_{16}\text{N}_8\text{Pt}$. In air, the thermal stability increased in the following order: $\text{H}_2\text{PtCl}_6 \cdot 4.4\text{H}_2\text{O} < \text{Pt}(\text{NH}_3)_4(\text{OH})_2 < \text{Pt}(\text{C}_5\text{H}_7\text{O}_2)_2 < \text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2 < \text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot 0.3\text{H}_2\text{O}$.

The unusually high thermal stability of platinum phthalocyanine is attributed to the resonance energy associated with the planar phthalocyanine structure. Further-

more, the coordinate and covalent bonding of the platinum atom located in the center of this molecule may also explain the observed thermal stability¹⁴. In contrast, the low affinity of Pt(II) for oxygen¹⁵ resulted in the poor thermal stability of $\text{Pt}(\text{C}_5\text{H}_7\text{O}_2)_2$ in a hydrogen environment. Pt(II) has a stronger affinity for nitrogen than oxygen¹⁶ and this is reflected in the higher thermal stability of the ammoniated Pt(II) compounds compared to $\text{Pt}(\text{C}_5\text{H}_7\text{O}_2)_2$.

Differential thermal analysis

A heating rate of $10^\circ\text{C min}^{-1}$ was used to conform to the heating rate from the TG investigation. This heating rate is the most commonly employed¹⁷ but may be much too fast to obtain reasonable heat transfer to the sample. Nevertheless, it was felt that qualitative information could be obtained under these conditions and taking into consideration the limitation discussed in the Experimental section.

A summary of the DTA results obtained on various platinum compounds is presented in Table 2. Because of the difference in the experimental conditions available, poor agreement was observed for the onset of thermal decomposition of the same platinum compound in the TG and DTA apparatuses. In general, the decomposition temperature recorded by DTA was higher than the temperature measured by TG.

TABLE 2

DTA STUDY OF PLATINUM COMPOUNDS

Platinum compound	Gas environment	Heats of reaction
$\text{Pt}(\text{NH}_3)_4\text{Cl}_2$	air	endothermic
$\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$	air	exothermic
	argon	exothermic
	hydrogen	exothermic
$\text{Pt}(\text{C}_5\text{H}_7\text{O}_2)_2$	air	endothermic
	hydrogen	exothermic

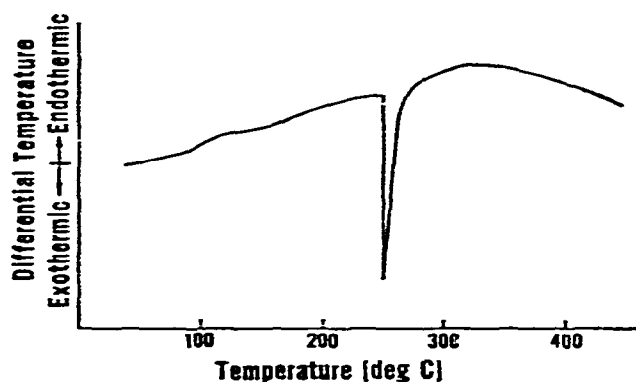


Fig. 6. DTA of platinum diamino dinitrite in air.

A DTA curve for the air decomposition of $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ is shown in Fig. 6. An exothermic reaction was evident at the decomposition temperature, which was very well-defined by a rapid, almost instantaneous release of heat. DTA curves of $\text{Pt}(\text{NH}_3)_2(\text{NO})_2$ obtained in argon and hydrogen showed similar characteristic sharp exothermic peaks.

The DTA results obtained with $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ in air were in qualitative agreement with the observations reported by Wendlandt⁹. Two endothermic peaks were observed in the DTA curve, corresponding to the step-wise thermal dissociation recorded with the microbalance.

Whereas the thermal dissociation of $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ in air and hydrogen was exothermic, $\text{Pt}(\text{C}_5\text{H}_7\text{O}_2)_2$ decomposed by an endothermic reaction in the former gas and an exothermic reaction in the latter. The presence of oxidizing groups (NO_3^-) in $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2](\text{NO}_3)_2$ was suggested by Wendlandt⁹ as responsible for the exothermic thermal decomposition of this compound in air. Similarly, the exothermic thermal dissociation of $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ in air may also be explained by the presence of an oxidizing group, NO_2^- .

REFERENCES

- 1 H. A. Benesi, R. M. Curtis and H. P. Studer, *J. Catal.*, 10 (1968) 328.
- 2 T. A. Dorling, B. W. J. Lynch and R. L. Moss, *J. Catal.*, 20 (1971) 190.
- 3 V. S. Boronin, V. S. Nikulina and O. M. Poltorak, *Russ. J. Phys. Chem.*, 37 (1963) 626.
- 4 K. Morikawa, T. Shirasaki and M. Okada, *Adv. Catal.*, 20 (1969) 97.
- 5 N. H. Sagert and R. M. L. Pointeau, *Can. J. Chem.*, 49 (1971) 3411.
- 6 A. E. Newkirk and D. W. McKee, *J. Catal.*, 11 (1968) 370.
- 7 *Gmelins Handbuch der anorganischen Chemie*, Verlag Chemie, Berlin, 8th ed., 1939, p. 77.
- 8 F. Figueras, B. B. Menciaer, L. Demourgues, C. Naccache and Y. Trambouze, *J. Catal.*, 19 (1970) 315.
- 9 W. W. Wendlandt, *Texas J. Sci.*, 14 (1962) 264.
- 10 B. P. Block, E. S. Roth and J. Simkin, *J. Inorg. Nucl. Chem.*, 16 (1960) 48.
- 11 R. G. Charles and M. A. Pawlikowski, *J. Phys. Chem.*, 62 (1958) 440.
- 12 E. C. Winslow and A. Laferriere, *J. Polymer Sci.*, 60 (1962) 65.
- 13 P. A. Barrett, C. E. Dent and R. P. Linstead, *J. Chem. Soc.*, (1936) 1719.
- 14 Frank H. Moser and Arthur L. Thomas, *Phthalocyanine Compounds*, Reinhold, New York, 1963, p. 12.
- 15 N. V. Sidgwick, *The Chemical Elements and Their Compounds*, Vol. II, Oxford University Press, London, 1962, p. 1600.
- 16 N. V. Sidgwick, *The Chemical Elements and Their Compounds*, Vol. II, Oxford, University Press, London, 1962, p. 1597.
- 17 Paul D. Garn, *Thermoanalytical Methods of Investigation*, Academic Press, New York, 1965, p. 61.