

## **THE THERMAL DECOMPOSITION OF PALLADIUM ACETATE\***

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The nature, products, and enthalpy of the thermal decomposition of  $[\text{Pd}(\text{CH}_3\text{CO}_2)_2]_3$  were determined in air, nitrogen and vacuum. Thermogravimetry, differential thermal analysis, evolved gas analysis, differential scanning calorimetry, and infrared spectroscopy were used to characterize the process and products. In vacuum the trimer volatilizes completely below 200 °C. The IR spectrum of the gas phase species is reported. At atmospheric pressure the material decomposed to Pd between 200 and 300 °C depending upon the rate of heating. The apparent activation energy for this process is about  $115 \pm 5 \text{ kJ mol}^{-1}$  and the enthalpy is  $440 \pm 20 \text{ kJ mol}^{-1}$ . In the presence of oxygen, however, oxidation of the ligands leads to an overall exothermic process. The resulting Pd then slowly oxidizes to  $\text{PdO}_2$  up to the decomposition temperature of the oxide near 800 °C. There is the slight loss of a Pd containing species, presumably due to sublimation or gas entrainment, during the decomposition below 300 °C. The extent of this loss increases with increasing heating rate, approaching 10% of the total Pd at heating rates of  $64 \text{ °C min}^{-1}$ .

The stoichiometry, mechanisms, and energetics of the thermal decomposition of palladium(II) acetate,  $[\text{Pd}(\text{CH}_3\text{CO}_2)_2]_3$ , are of considerable interest because of its potential use as a metallization precursor for integrated circuits [1]. This thermal decomposition reaction and characterization of the products were investigated by thermogravimetry (TG), differential thermal analysis (DTA), differential scanning calorimetry (DSC), mass spectrographic evolved gas analysis (EGA), infrared spectroscopy, and X-ray diffraction.

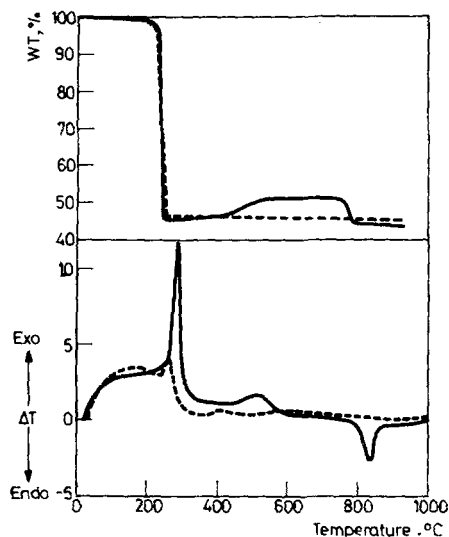
### **Experimental procedures and results**

The source of palladium(II) acetate was Aldrich Chemical Company (Lot 4509BL). This material was used without further purification.

The TG, DTA, and DSC results were obtained using Perkin-Elmer models TGS-4, DTA-1700, and DSC-4, respectively. The EGA apparatus has been

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described elsewhere [2] as has the digital data acquisition and processing system [3]. Figure 1 shows TG and DTA curves at  $16 \text{ deg min}^{-1}$  in air and  $\text{N}_2$ . Table 1 summarizes the weight loss immediately after the decomposition. To obtain the apparent activation energy for the decomposition process, TG experiments were performed at 64, 32, 16, 8, 4, and  $2 \text{ deg min}^{-1}$  using nominally the same size

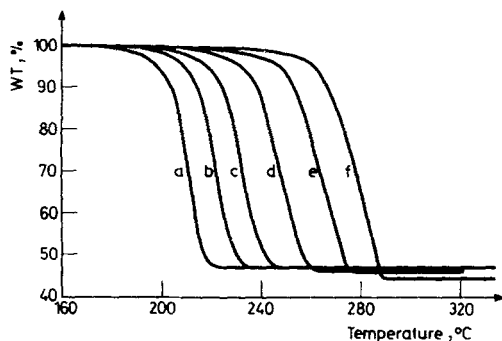


**Fig. 1** Thermal analysis of palladium(II) acetate,  $16 \text{ deg min}^{-1}$ . a) TG nitrogen 17.478 mg ----, air 16.415 mg; b) DTA nitrogen, 23.18 mg ----, air 23.40 mg

**Table 1** Weight loss for the thermal decomposition of palladium(II) acetate

Heating rate, $\text{deg min}^{-1}$	Atmosphere	% Wt Loss
		250°–300°, prior to oxidation
64	$\text{N}_2$	55.66
64	Air	57.20
32	$\text{N}_2$	54.11
32	Air	55.86
16	$\text{N}_2$	53.55
16	Air	54.91
8	$\text{N}_2$	53.16
8	Air	54.49
4	$\text{N}_2$	52.92
4	Air	53.57
2	$\text{N}_2$	52.90
2	Air	53.52

sample,  $17.4 \pm 1$  mg. Results obtained in  $N_2$  are presented in Fig. 2. Table 2 is a summary of the data selected for the Kissinger [4] method of kinetic analysis. In this method the apparent activation energy is derived from the slope of a plot of  $\log(\text{heating rate}/T_m^2)$  vs.  $1/T_m$ , where  $T_m$  is the temperature in degrees K at the maximum rate of decomposition. A plot of this data for  $N_2$  is shown in Fig. 3. The



**Fig. 2** Thermogravimetry of palladium(II) acetate in nitrogen. a) 2 deg  $\text{min}^{-1}$ , 17.553 mg; b) 4 deg  $\text{min}^{-1}$ , 16.471 mg; c) 8 deg  $\text{min}^{-1}$ , 17.721 mg; d) 16 deg  $\text{min}^{-1}$ , 17.478 mg; e) 32 deg  $\text{min}^{-1}$ , 17.146 mg; f) 64 deg  $\text{min}^{-1}$ , 16.587 mg

**Table 2** Input TG data for the Kissinger [4] kinetic analysis of the thermal decomposition of palladium(II) acetate

Heating rate, deg $\text{min}^{-1}$	Apparent temperature at the maximum decomposition rate, °C	
	$N_2$	Air
64	283	276
32	267	264
16	246	249
8	232	238
4	222	225
2	211	214

apparent activation energy is calculated from the slope of the least squares fit (line in Fig. 3) and found to be  $97 \text{ kJ mol}^{-1}$  ( $23 \text{ kcal mol}^{-1}$ ). The decomposition is highly exothermic in air as can be seen in Fig. 1. Consequently, there is significant thermal runaway or self-heating that distorts the apparent heating rate in the region of interest. The kinetic analysis of this data gives a calculated apparent activation energy that is about 25% greater.

The Ozawa [5] method of kinetic analysis for data obtained at different heating rates is more powerful in that values of apparent activation energy can be derived at any fraction reacted ( $\alpha$ ) during the reaction and hence, changes in mechanism that

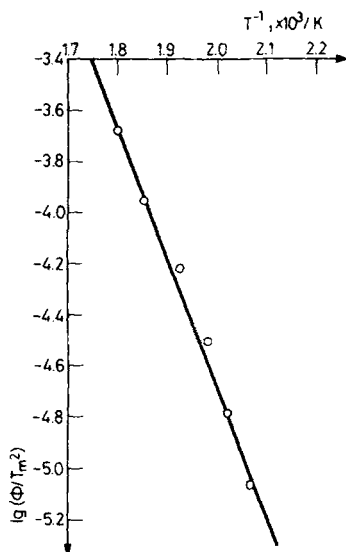
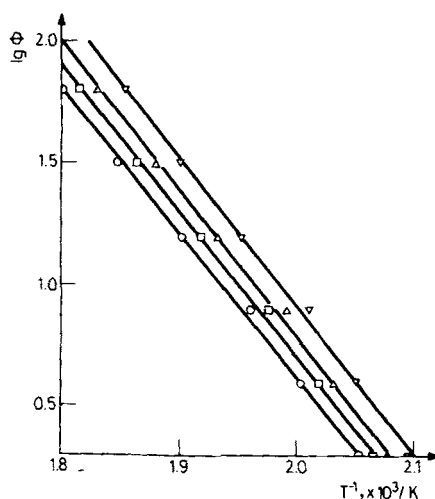


Fig. 3 Kissinger [3] kinetic analysis of the thermal decomposition of palladium(II) acetate in nitrogen (see Table 2). Apparent activation energy is  $97 \text{ kJ mol}^{-1}$   $23 \text{ kcal mol}^{-1}$  based upon the slope of the indicated least squares straight line. Heating rate ( $\text{K min}^{-1}$ ) =  $\emptyset$

might occur during the reaction may be detected. Data are summarized in Table 3 for selected fractions reacted. The data for runs in  $\text{N}_2$  are plotted in Fig. 4 according to the Ozawa method, i.e.,  $\log(\text{heating rate})$  vs.  $1/T_\alpha$ , where  $T_\alpha$  is the temperature in degrees K corresponding to selected fractions reacted. The values of the apparent

Table 3 Input data for the Ozawa [5] kinetic analysis of thermal decomposition of palladium(II) acetate

Heating rate, deg min <sup>-1</sup>	Atmosphere	Apparent temperature at the indicated fraction reacted, °C			
		$\alpha = 0.2$	0.4	0.6	0.8
64	N <sub>2</sub>	266.1	272.8	278.0	282.3
32	N <sub>2</sub>	253.0	258.5	263.6	268.4
16	N <sub>2</sub>	238.8	244.0	248.0	252.5
8	N <sub>2</sub>	224.0	229.3	232.9	236.9
4	N <sub>2</sub>	214.0	218.8	222.2	226.0
2	N <sub>2</sub>	203.6	298.4	211.3	214.6
64	Air	263.7	269.2	273.0	275.7
32	Air	251.5	256.8	260.9	263.6
16	Air	239.7	244.1	247.8	249.4
8	Air	227.4	231.2	239.0	237.5
4	Air	215.7	220.0	222.8	226.6
2	Air	210.0	212.7	214.7	217.4



**Fig. 4** Ozawa [4] kinetic analysis of the thermal decomposition of palladium(II) acetate in nitrogen (see Tables 3 and 4). Straight lines are least squares fit to each set of 6 points. Heating rate ( $\text{deg min}^{-1}$ ) =  $\emptyset$ .  $\circ$  Fraction reacted = 0.8;  $\square$  Fraction reacted = 0.6;  $\triangle$  Fraction reacted = 0.4;  $\nabla$  Fraction reacted = 0.2

activation energy, calculated from the slopes of the least squares fits, are presented in Table 4, giving an average value of  $115 \text{ kJ mol}^{-1}$  ( $27.4 \text{ kcal mol}^{-1}$ ). Analysis of the data in air yields values about 25% higher but are suspect owing to the effects of self-heating.

The DSC curves are presented in Fig. 5. The assumed base lines used for integration of the curves are also shown. Table 5 lists the calibration constants to be applied to these curves for both temperature and energy derived under the same experimental conditions, in  $\text{N}_2$ , for the melting of In, Sn, and Pb. The average

**Table 4** Results of the Ozawa [5] kinetic analysis for the thermal decomposition of palladium(II) acetate in nitrogen

Fraction reacted $\alpha$	Apparent activation energy	
	$\text{kJ mol}^{-1}$	$\text{kcal mol}^{-1}$
0.2	116	27.8
0.4	116	27.7
0.6	113	27.1
0.8	113	27.0
Avg.	115	27.4

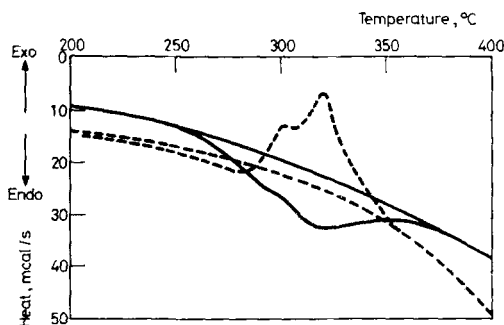


Fig. 5 DSC curves for palladium(II) acetate at heating rate of 20 deg min<sup>-1</sup>. — nitrogen, 4.72 mg; ----, air 5.53 mg

Table 5 Calibration factors for the DSC data

Metal	Energy factor <sup>a</sup>	Melting temperature		°C, $\Delta T$
		measured <sup>b</sup>	reported <sup>b</sup>	
Indium	1.08 <sub>1</sub>	171.6	156.6	+15.0
Tin	1.05 <sub>5</sub>	248.7	232.0	+16.7
Lead	1.10 <sub>5</sub>	339.0	327.5	+11.5
	Avg.	1.08		

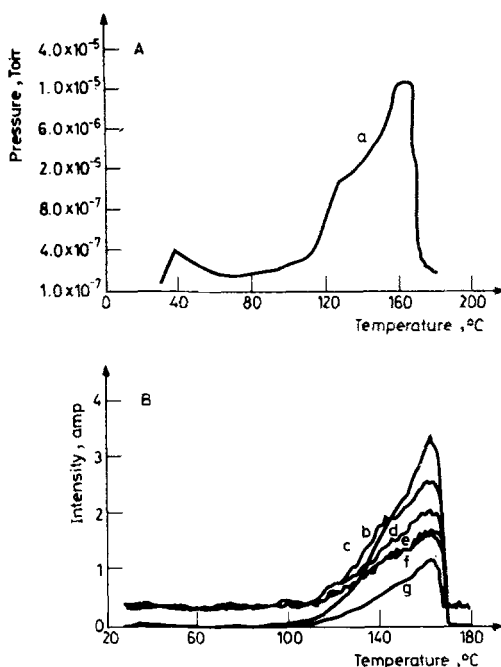
<sup>a</sup> Scale correction factor, i.e., reported [9]  $\Delta H = (\text{factor}) (\text{measured } \Delta H)$ .

<sup>b</sup> Extrapolated onset.

energy factor of 1.08 was used to correct the areas derived from Fig. 5. The resulting values of enthalpy for the decomposition are +440 kJ mol<sup>-1</sup> (106 kcal mol<sup>-1</sup>) in N<sub>2</sub> and -340 kJ mol<sup>-1</sup> (-81.5 kcal mol<sup>-1</sup>) in air. X-ray powder diffraction patterns of the residues from these two DSC experiments show that the product at 500° in N<sub>2</sub> was entirely Pd and in air was about equal amounts of PdO and Pd.

During EGA experiments, the radiant heating from the ionizing filaments of the mass spectrometer is generally enough to heat the sample to ~175°, albeit in a nonlinear fashion. A linear controlled heating rate is difficult to achieve in this temperature region. Fortunately, this radiant heating by the filaments, as opposed to the normal furnace/controller mode, was adequate for the purposes of this work. Plots of the total pressure and the intensities associated with selected mass peaks as a function of temperature are shown in Fig. 6. The sample preweighed into an alumina crucible, completely vaporized after heating to ~175° in the base vacuum of  $1 \times 10^{-7}$  torr (i.e., absence of outgassing).

Sublimation experiments were carried out in vacuum at a base pressure of  $4 \times 10^{-4}$  torr. Sublimation of palladium(II) acetate begins at 145°, with some decomposition to the metal observed.



**Fig 6** EGA of palladium(II) acetate at heating rate of  $10 \text{ deg min}^{-1}$ . a) Total pressure  $\mu$ ; b)  $\text{Pd}(\text{CH}_3\text{COO})_2^+$  AMU =  $224 \text{ amp} \times 10^9$ ; c)  $\text{CH}_3\text{COO}^+$  AMU =  $57 \text{ amp} \times 10^9$ ; d)  $\text{PdCH}_3\text{COO}^+$  AMU =  $165 \text{ amp} \times 10^9$ ; e)  $\text{Pd}^+$  AMU =  $106 \text{ amp} \times 10^9$ ; f)  $\text{PdO}^+$  AMU =  $122 \text{ amp} \times 10^9$ ; g)  $\text{CH}_3\text{CO}^+$  AMU =  $.43 \text{ amp} \times 10^6$

## Discussion

The pathways of the thermal decomposition of palladium(II) acetate can be derived from the X-ray diffraction results and the thermoanalytical data summarized in Table 1 and Figs 1 and 6. The theoretical values for the weight loss on conversion of palladium(II) acetate to palladium(II) oxide and palladium metal are 45.48% and 52.60%, respectively. In the inert atmosphere at slower rates, the weight loss approaches the theoretical weight loss for the formation of palladium. In air the weight losses are somewhat higher. Since the observed weight losses are greater than the calculated value, these differences can not be explained by incomplete decomposition or the formation of some palladium(II) oxide. There must be some volatilization of a palladium-containing species. This is consistent with the sublimation experiments and observation during the EGA experiments that the sample was completely volatilized in vacuum below  $200^{\circ}$ . The EGA plots in Fig. 6 clearly show the presence of vaporized palladium acetate species at these temperatures.

A recent study also finds that the trimer vaporizes intact at 230° in argon and at 155° in the vacuum of a mass spectrometer [6]. Thermoanalytical studies of other metal acetates suggest that acetic acid is the dominant organic by-product of decomposition in those cases where pure metal is formed. Those acetates whose decomposition produces metal oxides yield acetone as the dominant organic by-product [7, 8].

An infrared spectrum of the volatile products resulting from decomposition of palladium(II) acetate in vacuum shows the presence of acetic acid and carbon dioxide, but not acetone. Clearly, to account for the reduction to palladium, other volatile species must also be formed, although these were not detected in our experiments. The greater weight loss with increasing heating rate at atmospheric pressure suggests that only partial decomposition of the palladium acetate occurs before reaching the sublimation temperature. In vacuum, however, the EGA results show that sublimation precedes decomposition. The increased weight loss observed in air vs. nitrogen may be due to the self-heating effect resulting from oxidation of the organic material. The exothermic nature of the decomposition, shown in Fig. 1b, leads to intense local heating that accelerates the rate of sublimation of palladium(II) acetate.

After the decomposition to elemental palladium, further heating in air leads to a slow oxidation to form palladium(II) oxide, PdO. At heating rates of  $\leq 16 \text{ deg min}^{-1}$  this reaction is virtually complete, based on the weight gain of about 7% (Fig. 1a). This oxidation is also evident in the DTA curve as an exotherm around 500°. The palladium(II) oxide can be reduced back to the metal by heating beyond 800°. Consistent with this, we find sizable amounts of palladium(II) oxide in the DSC residue of the sample heated to 500° in air, as determined by X-ray diffraction.

In the kinetic interpretation of the TG data certain caveats must be noted, arising from two factors noted earlier, i.e., the tendency of the sample to self-heat on oxidation and the overlap between the decomposition and sublimation processes. The atmospheric effects on the decomposition are summarized by the data in Tables 2 and 3. At the slower heating rates, the temperature at the maximum rate of decomposition (Table 2) or at each fraction reacted (Table 3) is greater in air than in N<sub>2</sub>. The reverse is true at the higher rates. Apparently the process is slightly inhibited by air at slow heating rates, where the additional heat generated by the oxidation of the organic material can be more easily dissipated. At the faster heating rates this extra heat leads to a thermal runaway so that the apparent temperature measured by the nearby thermocouple is a less accurate indication of the true temperature of reaction.

In comparing the Kissinger and Ozawa approaches the value of  $\alpha$  at the point of maximum decomposition rate is changing with heating rate based on a comparison



of the apparent temperature in Table 2 with those in Table 3. At the faster heating rates the maximum decomposition rate occurs near the end of the reaction while at the slower heating rates the decomposition rate is more symmetrical with respect to the amount decomposed. In spite of these caveats, the apparent activation energy derived from the Ozawa analysis shows only a small shift with choice of the fraction reacted. The lines in Fig. 4 are nearly parallel and hence, the calculated values of apparent activation energy in Table 4 vary less than 3%. Because of the changing fraction reacted at the maximum decomposition rate, the value of  $97 \text{ kJ mol}^{-1}$  derived from the Kissinger method of analysis is considered less reliable than the average value of  $115 \text{ kJ mol}^{-1}$  obtained by the Ozawa method of analysis.

The DSC curve in nitrogen shows that decomposition of palladium(II) acetate to palladium metal is endothermic and occurs in a multistep process, as is evident from the shoulder present on the low temperature side of the peak (see Fig. 5). The total area under the curve corresponds to  $440 \pm 20 \text{ kJ mol}^{-1}$ , using the average correction factor in Table 4 derived from In, Sn, and Pb standards. The data summarized in Table 4 also suggest that the experimental temperature scale used in Fig. 5 should be revised downward by about  $14^\circ$ .

In air, the overall decomposition reaction is exothermic, with an enthalpy of  $-340 \pm 20 \text{ kJ mol}^{-1}$ . This value, however, is not particularly relevant since it depends on the extent to which oxidation of the organic material takes place within the detectability of the sensor. It does set a lower limit of  $-780 \pm 40 \text{ kJ mol}^{-1}$  on the enthalpy for the oxidation of the organic products. The data in Fig. 1 show that the oxidation of the palladium is not yet a factor at the decomposition temperature.

## Conclusions

1. The sublimation and decomposition of palladium(II) acetate occur at similar temperatures. At slow heating rates in vacuum all the material sublimates before it decomposes. At atmospheric pressures the exact amount of palladium that is lost via volatilization depends on the heating rate and the extent of exothermic oxidation that occurs. In both air and nitrogen the solid product is palladium. On further heating in air, the metal is oxidized to palladium(II) oxide, which finally dissociates at higher temperatures to reform palladium.

2. The enthalpy associated with the thermal decomposition at  $10 \text{ deg min}^{-1}$  in nitrogen is determined to be  $440 \pm 20 \text{ kJ mol}^{-1}$ . The decomposition in air is highly exothermic but the exact value depends on the extent to which the oxidation of the organic products is detected. A single symmetrical peak is not observed in either atmosphere confirming the multistep nature of the process.

3. The apparent activation energy for the rate of thermal decomposition in

nitrogen was determined from TG curves obtained at 6 heating rates from 2 to 64 deg min<sup>-1</sup>. The Ozawa method of kinetic analysis was used for four different extents of reaction,  $\alpha = 0.2, 0.4, 0.6$  and  $0.8$ . An average value of 115 kJ mol<sup>-1</sup> was measured in nitrogen, with little variation for the different values of  $\alpha$ . The Kissenger method of analysis was also used but it was judged to give a less reliable result. The self-heating (thermal runaway) resulting from the oxidation of the organic material makes the kinetic data in air unreliable.

4. Infrared spectroscopy and EGA indicate that acetic acid and carbon dioxide are the primary by-products of palladium(II) acetate decomposition. We did not detect any other volatile products that, nevertheless, must be formed in order to completely account for reduction of the palladium and formation of acetic acid.

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**Zusammenfassung** — Natur, Produkte und Enthalpie der thermischen Zersetzung von  $[\text{Pd}(\text{CH}_3\text{CO}_2)_2]_3$  in Luft, Stickstoff und Vakuum wurden untersucht. Zur Charakterisierung des Prozesses und der Produkte wurden TG, DTA, EGA, DSC und IR-Spektroskopie herangezogen. Im Vakuum verflüchtigt sich das Trimere vollständig unterhalb 200°. Das IR-Spektrum der gasförmigen Species ist angegeben. Bei Atmosphärendruck zersetzt sich das Material, abhängig von der Aufheizgeschwindigkeit, zwischen 200 und 300° zu Pd. Die scheinbare Aktivierungsenergie für diesen Prozeß beträgt  $115 \pm 5$  kJ · mol<sup>-1</sup>, die Enthalpie beläuft sich auf  $440 \pm 20$  kJ · mol<sup>-1</sup>. In Gegenwart von Sauerstoff werden die gasförmigen Produkte sofort oxydiert, was ein exothermen Bruttoeffekt zur Folge hat. In Gegenwart von Sauerstoff wird Pd langsam bis zur Zersetzung des Oxids bei nahe 800° oxydiert. Es wird ein geringer Verlust einer Pd enthaltenden Species beobachtet, der vermutlich auf Sublimation oder auf Mitreißen im Gasstrom während der Zersetzung unterhalb 300° zurückzuführen ist. Dieser Verlust wird mit der Erhöhung der Aufheizgeschwindigkeit größer und erreicht bei einer Aufheizgeschwindigkeit von 64° · min<sup>-1</sup> 10% des Gesamt-Pd.

**Резюме** — В атмосфере воздуха, азота и в вакууме изучен характер термического разложения ацетата палладия  $[\text{Pd}(\text{CH}_3\text{CO}_2)_2]_3$ , а также определены продукты разложения и энтальпия реакции. Процесс разложения и идентификация образующихся продуктов были проведены с помощью ТГ, ДТА, АВГ, ДСК и ИК спектроскопии. В вакууме тример ацетата палладия

полностью улетучивается при температуре ниже  $200^{\circ}$ . Приведен ИК спектр газообразных частиц. При атмосферном давлении вещество разлагается до палладия между  $200$  и  $300^{\circ}$  в зависимости от скорости нагрева. Кажущаяся энергия активации процесса разложения составляет около  $155 \pm 5$  кдж  $\cdot$  моль $^{-1}$ , а энтальпия —  $440 \pm 20$  кдж  $\cdot$  моль $^{-1}$ . Однако, в присутствии кислорода газообразные продукты сразу же окисляются, приводя тем самым к полностью экзотермическому процессу. В присутствии кислорода палладий медленно окисляется вплоть до температуры разложения окисла около  $800^{\circ}$ . Во время разложения ацетата палладия ниже  $300^{\circ}$  происходила небольшая потеря палладия, что, по видимому, обусловлено сублимацией его или же уносом газом. Степень потери увеличивалась при увеличении скорости нагрева и составляла 10% общего количества палладия при скорости нагрева  $64^{\circ}$  в минуту.