edible oils can be hydrogenated with the above mentioned catalyst system. Table 1 represents the hydrogenation of soyabean oil using acetic acid as solvent. Here, the catalyst system has a remarkable preference for the hydrogenation of linoleic acid. As long as some linoleate is present, hardly any linolenate is hydrogenated. In addition, the catalyst has a considerable selectivity for the formation of oleate. As appears from the trans content, isomerization of the double bonds also takes place here. Methyl esters from soyabean oil give more or less the same picture.

As solvents, the fatty acid homologs from acetic acid to stearic acid inclusive have been investigated. In all cases the catalyst was active. Other suitable solvents are ketones such as acetone, methyl ethyl ketone, and diethyl ketone, as well as a number of ethers such as diethyl ether, and dipropyl ether, tetrahydrofuran, and nitrobenzene.

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Kinetics of the Low Pressure Nitrous Oxide Decomposition on Iridium and Palladium Filaments

INTRODUCTION

The catalytic decomposition of nitrous oxide has been investigated on various metals and metal oxides (*1*, *2*). In this paper, the decomposition kinetics on iridium and palladium are reported.

EXPERIMENTAL

Apparatus. The experimental setup is the same as that previously described in ref. (*2*). Essentially, it consists of a gas-handling system for purification and storage of gases and a reactor flask in which the filament is mounted. The reactor is connected to a mass spectrometer which in turn monitors the reaction. The apparatus is given a modest bake-out (250°C) before a run while Vac-ion pumping is used to reduce the pressure in the system to at least 10^{-8} torr. A mass spectrometer is directly connected to the reactor through a by-pass valve to detect leaks and analyze gases desorbed from the filament when it is flashed before a run.

Materials. The gases (N_2O, N_2, and O_2) were commercially available and purified by freezing out the impurities in liquid nitrogen or Dry Ice cold traps.

The calculated surface areas of the filaments are given in the tables; they are in the range of 1 cm^2.

RESULTS

1. Iridium Filaments

a. Decomposition kinetics. The decomposition on iridium has been found to fit the following rate equation:

$$-dP_{\mathrm{N_2O}}/dt = k_{\mathrm{app}}(P_{\mathrm{N_2O}}/P_{\mathrm{O_2}}^{1/2}) \qquad (1)$$

where k_{app} is the apparent rate constant. This equation is an example of the Langmuir-Hinshelwood kinetics with strong poisoning by the product, in this case atomic oxygen. The data from such runs has been plotted according to Eq. (1) by the procedure outlined in ref. (*2*), and the rate constants have been obtained from the slopes of these plots. These results are presented in Table 1 where the data indicates fair reproducibility. The proposed kinetics may also be verified by using the integrated rate equation. Integrating Eq. (1) gives

TABLE 1

Decomposition on Iridium

T (°K)	P_{N2O} ($\mu^{1/2}$/min)	Half-life (min)	k_{app}[a] ($^{1/2}$/min)
Iridium Filament No. 1		*Surface area 0.9 cm²*	
1175°	74	24.8	0.123
1175°	121	31.5	0.105
1260°	124	7.7	0.365
1260°	125	8.5	0.350
1344°	32	2.0	0.83
1344°	62	2.7	0.86
1344°	112	3.0	1.10
1344°	122	3.15	1.05
1344°	220	4.5	1.00
1344°	425	6.5	1.11
1344°	784	8.7	0.84
1344°	1332	11.4	0.96
Iridium Filament No. 4		*Surface area 2.52 cm²*	
1008°	106	—	0.027
1088°	108	51.7	0.07
1098°	97	37.0	0.10
1111°	115	25.2	0.148
1162°	129	12.9	0.27
1242°	109	5.2	0.66
1288°	130	3.0	1.17
1310°	143	2.2	1.58

[a] Multiply k_{app} by 1.1×10^8 and divide by surface area of the filament to convert into units of (molecules/cc)$^{1/2}$ sec^{-1} cm^{-2} for a 1-cc reactor.

$$a^{1/2} \ln \left(\frac{a^{1/2} + x^{1/2}}{a^{1/2} - x^{1/2}} \right) - (2a)^{1/2} = k_{\mathrm{app}}t \qquad (2)$$

where a equals the starting pressure of nitrous oxide and x corresponds to the pressure of nitrous oxide which has decomposed. At the half-life ($t_{1/2}$), the above equation reduces to

$$(0.348/k_{\mathrm{app}})a^{1/2} = t_{1/2} \qquad (3)$$

Thus, a plot of the half-life versus the square root of the initial pressure for a series of runs at constant temperature should be linear with the intercept passing through the origin. This has been found to be the case for the series of runs at 1344°K listed in Table 1.

b. Apparent energy of activation. It is possible to obtain an apparent activation energy by an Arrhenius plot of the apparent rate constant or the reciprocal of the half-life values. From such plots an activation energy of 40 ± 2 kcal/mole has been obtained. The k_{app} or $t_{1/2}$ values in Table 1 are normalized to a cm² filament surface area and correspond to an initial nitrous oxide pressure of approximately 120 μ. The data point scatter from such plots is reasonably good, and since the surface areas of these filaments differ by a factor of over 2½, it does not appear that secondary surface effects are complicating the kinetics. It should also be noted that in Table 1 the reaction rate values are consistent for runs conducted at the same temperature. In addition the rate data are in good agreement between different filaments over the same temperature range. This points out that the change in the surface area of the filaments due to "roughness" is not significant.

c. Added oxygen. A brief investigation of the effect of added oxygen on the reaction has been made. The results are listed in Table 2. As expected, the addition of oxygen definitely poisons the reaction. However, more work is needed to clearly establish whether added oxygen is as effective a poison as product oxygen. Because of the relative high temperature (1375°K) and pressure of the added oxygen (to 360 μ) for this series of experiments, some iridium evaporates from the filament as iridium oxide depositing as a black coating on the reactor walls. Since the reactor walls are at room temperature, the deposited iridium basically did not interfere with the reaction kinetics. In addition, some

TABLE 2
EFFECT OF ADDED O_2 ON NITROUS OXIDE DECOMPOSITION

T (°K)	P_{N_2O} (μ)	P_{O_2} added (μ)	Half-life (min)
Iridium Filament No. 3		*Surface area 1.23 cm²*	
1375°	175	—	2.3
1375°	165	25	2.9
1375°	172	360	10.5
Palladium Filament No. 2		*Surface area 1.03 cm²*	
1101°	113	—	4.5
1101°	100	61.5	14
1101°	100	125	22.5

carbon dioxide is produced which interferes with the mass analysis for nitrous oxide. This carbon dioxide is thought to result from the interaction of oxygen with the carbon in the tungsten filament supports which is due to the relatively high temperature at which these experiments were conducted.

2. *Palladium Filaments*

Decomposition kinetics. In Table 3 the results are tabulated for the decomposition study on the palladium filaments. The reaction is poisoned by molecular oxygen, and the rate data has been found to fit the following Langmuir-Hinshelwood equation:

$$-dP_{N_2O}/dt = k_0K_1P_{N_2O}/(1 + K_2P_{O_2}) \quad (4)$$

where k_0 is the true rate constant and k_1 and k_2 are the adsorption equilibrium constants for nitrous oxide and oxygen, respectively. Integrating the above equation and rearranging it gives

$$\left(\frac{x}{t}\right) = \left(\frac{2 + a}{K_2}\right)\frac{1}{t}\ln\left(\frac{a}{a - x}\right) - \frac{2k_0K_1}{K_2} \quad (5)$$

the symbols have been previously identified. Figure 1 shows a typical plot of the data according to Eq. (5); the values of k_0K_1 and K_2 are obtained from the slope, intercept, and initial pressure of nitrous oxide.

TABLE 3
DECOMPOSITION ON PALLADIUM

T (°K)	P_{N_2O} (μ)	Half-life (min/cm²)	$k_0K \times 10^{2a}$ (sec⁻¹)	K_2^b (−1) (μ)
Palladium Filament No. 1			*Surface area 1.0 cm²*	
1013°	139	13.0	0.466	0.228
1043°	165	8.4	0.72	0.20
1073°	204	7.0	0.734	0.12
1098°	210	5.2	1.45	0.20
1123°	124	2.40	1.23	0.098
1153°	218	2.5	2.20	0.110
1193°	138	1.33	2.56	0.06
Palladium Filament No. 2			*Surface area 1.03 cm²*	
1029°	109	12.9	0.592	0.408
1077°	116	6.2	0.669	0.169
1101°	113	4.45	0.78	0.141
1136°	120	3.2	1.46	0.203
1138°	115	2.9	1.32	0.154
1217°	120	1.2	2.775	0.116

[a] Multiply k_0K_1 by 1170 and divide by surface area of filament to convert into units of sec⁻¹ cm⁻² for a 1-cc reactor.

[b] Multiply K_2 by 3.11×10^{-11} to convert into units of (molecules/cc)⁻¹.

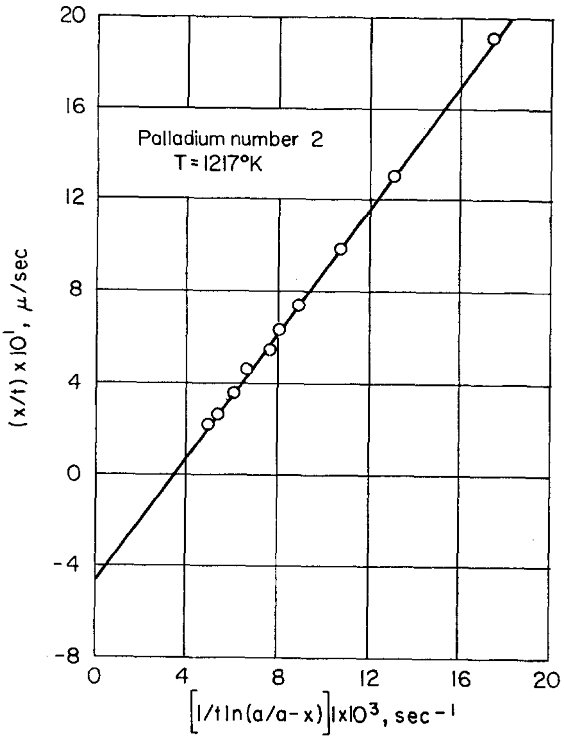

FIG. 1. Data from a typical nitrous oxide decomposition run on a palladium filament are plotted according to Eq. (5), the integrated rate equation.

b. Apparent energy of activation and heat of O_2 adsorption. The half-life values in Table 3 are normalized to a 1-cm^2 surface area. When the logarithm of the reciprocal half-life is plotted against the inverse temperature, an apparent activation energy of 30 ± 2 kcal/mole is obtained from the slope of this Arrhenius plot.

It is possible to obtain a value for the heat of oxygen adsorption by plotting the logarithm of K_2 values in Table 3 against the reciprocal of the temperature. An approximate value of 12 ± 3 kcal/mole is obtained from the slope of the Clausius-Clapeyron plot. This value obtained for heat of adsorption is consistent with the picture of an oxygen-poisoned surface where the heat of oxygen adsorption on a fully covered surface would be expected to be relatively low.

c. Added oxygen. Again a brief investigation of the effect of added oxygen on the reaction rate has been made. Added oxygen has been found to retard the reaction; this is evident in Table 2 where the half-life values are listed and found to increase with oxygen content. In order to determine if added oxygen has the same poisoning effect as product oxygen, the reaction rate data for the three runs listed in Table 2 have been plotted according to Eq. (4). According to this equation, the curves for the three runs should coincide. It has been found that within experimental error these curves do overlap. Thus, it has been concluded that added oxygen has the same poisoning effect as product oxygen.

An examination of the reaction rates for the decomposition on palladium and iridium and the previous work on platinum shows that the order of catalytic activity is Pd > Pt > Ir. This is in line with the other kinetics results where a comparison of rate equations indicates that oxygen is most strongly adsorbed on iridium and least effective on palladium. The poisoning by oxygen is intimately tied in with the ability of the metal to form stable metal oxide films plus the catalytic activity of that layer.

This characteristic is probably related to a common fundamental property of these metals but more work is needed to establish this assumption.

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Surface Composition of Equilibrated Copper-Nickel Alloy Films

Previous work (*1–3*) on copper-nickel alloy films equilibrated at 200°C confirmed the existence of a wide miscibility gap at this temperature. In agreement with thermodynamic data an alloy phase I ($\approx$20 at. % Ni) coexists with a phase II ($\geqslant$95 at. % Ni). Moreover, evidence was found suggesting that for films prepared by subsequent vacuum deposition of the two metals, followed by sintering at 200°C,