ular products hydrogen and hydrogen peroxide nor the free radicals hydrogen and hydroxyl are generated in equal numbers. Their experimental data clearly demonstrate that $G^{M}_{H_2O_2} > G^{M}_{H_2}$ so their eq. 5a and 5b could be replaced by reactions 2 and 3 of this paper. In their terminology $G^{M}_{H_2O_2}$ and $G^{M}_{H_2}$ are the primary molecular hydrogen peroxide and hydrogen yields, respectively. The hydrogen peroxide in excess of hydrogen is formed by reaction 3. While the Dainton–Sutton treatment is more general, the present results demonstrate that from *p*H 3.0 to a *p*H of 11.6 molecular hydrogen and hydrogen peroxide are formed in equimolar amounts. Therefore it is preferable to retain reaction 2 and use reaction 3 only at *p*H's below 3.0.

It is possible that reaction 3 originating only at high hydrogen ion concentration is brought about by stabilization of hydrogen atoms through the reaction

$$H + H^+ = H_2^+$$

employed by Rigg, Stein and Weiss[7] to explain the *p*H effect on the oxidation of ferrous sulfate. If the hydrogen molecule ion is more stable than the hydrogen atom toward recombination, one would expect a decrease in $G_{(1)}$ and in $G_{(2)}$, more favorable conditions for hydroxyl radical recombination, and a tendency toward a greater over-all yield of water decomposition. The total molecular hydrogen peroxide yield, $G^{M}_{H_2O_2}$, is obtained by taking one-half the sum of $G_{(2)} + G_{(3)}$ in the present work. In 1 *N* sulfuric acid at *p*H 0.32 this value is 0.86 and may be compared with $G^{M}_{H_2O_2}$ of 0.54–0.93 reported by Dainton and Sutton. (Adjustment of this range to a $G_{Fe^{+++}}$ of 15.5 has been made.) To a first approximation then the molecular hydrogen peroxide yield is independent of solute. Reaction 3 and to minor extents reactions 1 and 2 are dependent on hydrogen ion concentration. However, the total number of water molecules forming molecular products and free radicals capable of reacting with formic acid and by γ-rays is substantially independent of *p*H. This result is expected in view of the high average energy required per water molecule reacted (about 25 e.v. compared to the small free energy changes in the water produced by hydroxyl and hydrogen ions) and the great preponderance of water molecules present in these solutions.

Acknowledgment.—The technical assistance of Miss P. D. Walsh is gratefully acknowledged.

LEMONT, ILLINOIS

---

[7] T. Rigg, G. Stein and J. Weiss, *Proc. Roy. Soc.* (*London*), **A211**, 375 (1952).

[CONTRIBUTION FROM THE JAMES FORRESTAL RESEARCH CENTER, PRINCETON UNIVERSITY]

The Decomposition of Ammonia on Ruthenium, Rhodium and Palladium Catalysts Supported on Alumina

BY AKIRO AMANO AND HUGH TAYLOR

RECEIVED MARCH 1, 1954

The decomposition of ammonia on ruthenium, rhodium and palladium catalysts supported on alumina has been studied with ammonia alone and admixed with hydrogen or nitrogen or both. Nitrogen is without influence, but hydrogen inhibits the decomposition more pronouncedly with palladium than with ruthenium. With ruthenium the kinetic expression is $-d[NH_3]/dt = k[NH_3]^{0.6}[H_2]^{-0.9}$. An observed activation energy of 30.5 kcal. is obtained. Decompositions between 2 and 10% are attained in the temperature interval 350–400°. With rhodium such decomposition occurs between 360 and 450°, in absence and presence of hydrogen, with an observed activation energy of *ca.* 30 kcal. With palladium this extent of decomposition is first secured in the temperature range 510 to 570° with an activation energy in the neighborhood of 31.6 kcal. The relation of these results to findings of Trapnell and Kemball is discussed and the unsolved problem of specificity in catalysis is emphasized.

Chemisorption processes involved in catalytic reactions are at the heart of the catalytic problem and the science involved in the chemisorptive association between reactant and surface is still in a highly rudimentary state. A sequence of communications is planned sharply to reveal differences in specificity in a series of elementary catalysts and a few chosen simple chemical reactants so that the direction in which further advances in our knowledge may be secured will be indicated. The present work is concerned with the marked differences between ruthenium, rhodium and palladium, supported on alumina, as catalysts for the decomposition of ammonia. The results communicated indicate that the behavior of these elements in a trio of transition metals parallels the behavior that can be deduced from observations on iron and nickel, and on osmium and platinum in the two other series of Group VIII metals.

Experimental

Experimental Procedure.—The apparatus and procedure were similar to those used by Love and Emmett[1] in work with synthetic ammonia catalysts. A flow system at approximately one atmosphere was employed. Mixtures of ammonia, hydrogen and nitrogen in varying proportions were led through the catalyst bed at controlled velocities and temperatures. The undecomposed ammonia was absorbed in sulfuric acid and decomposition measured by the difference between the inlet and outlet ammonia. Capillary flowmeters, thermostated at 30°, with di-*n*-butyl phthalate as the flowmeter liquid, and calibrated with wet gas meters or, in the case of ammonia, with sulfuric acid were used to measure the flow velocities.

Materials Used.—Synthetic ammonia (Matheson) was used after drying over potassium hydroxide. Nitrogen and hydrogen from cylinders passed through purification trains of potassium hydroxide, hot copper at 480°, calcium chloride and phosphorus pentoxide.

The reactor was a glass tube 30 cm. long, 2.8 cm. inside diameter. The catalyst layer was 1.5 cm. deep in the

---

[1] K. S. Love and P. H. Emmett, THIS JOURNAL, **63**, 3297 (1941).

center of the tube with glass wool above and below, the upper wool acting as a preheater. A thermo-well at the center of the catalyst layer was used to define temperature with chromel–alumel thermocouples. The electric furnace, serving as heater, was hand-regulated, and was of sufficiently large heat capacity that temperatures constant within 0.5° could be maintained.

The catalysts were prepared by Baker and Co. and consisted of 0.5% by weight of ruthenium, rhodium and palladium on alumina pellets, cylindrical in shape, 3 mm. in length and diameter. The metal catalyst formed a black outer skin on the pellets which, inside, were white and essentially free from metal. The bulk density of the pellets was approximately 0.913.

Analysis.—Product gas was collected in a train of absorbing flasks each containing 100 cc. of approximately 0.75 *N* sulfuric acid. The time necessary to neutralize the acid in the first flask was measured and corrections were made for the change in concentrations of the acid in the second and third flasks. Tetrabromophenolsulfonphthalein was used as indicator. The sulfuric acid in the absorbing flasks was constantly agitated by a stream of nitrogen gas. This agitation minimizes variations in concentration in the absorbent. It served also to regulate back pressures arising from changing flow rates and smooths out the gas stream when several bottles are used, permitting closer regulation of the flow meters. The procedure gave satisfactory reproducibility between 2 and 10% decomposition of the ammonia.

Experimental Results

Reproducible results over periods extending to 10 hours under uniform conditions have been obtained. Initially the catalysts were reduced in hydrogen for 15 hours at 450° and 5 hours at 400° and then allowed to cool. Only in the initial run with each catalyst where there had been no previous contact with ammonia was there any anomaly in the rate of decomposition. Between individual runs the catalyst was reduced for 2 hours at 450° in hydrogen. After each such reduction the rate of decomposition rose gradually but after 3 hours this rate became constant and reproducible. This trend is indicated by the following data which also indicate the reproducibility of an experiment.

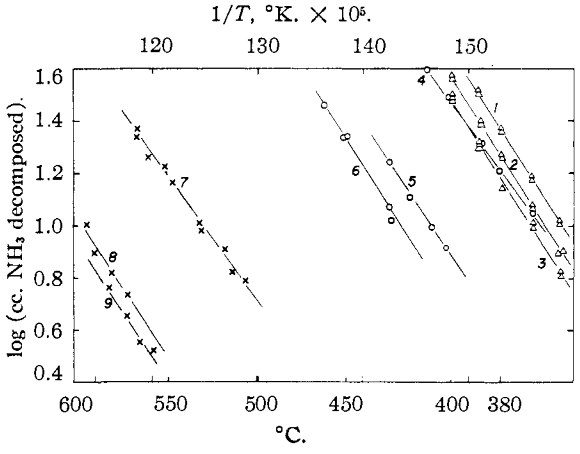

Fig. 1.—log NH_3 dec. *vs.* $1/T$:

		cc./min.	$E_{act.}$, kcal./mole
Ru, Δ	1	NH_3, 300; H_2, 300; N_2. 200	30.65
	2	NH_3, 300; H_2, 400; N_2, 100	30.65
	3	NH_3, 300; H_2, 500; N_2, ---	30.28
Rh, O	4	NH_3, 300; H_2, ---; N_2, 300	25.89
	5	NH_3, 300; H_2, 100; H_2, 200	27.90
	6	NH_3, 300; H_2, 200; N_2, 100	31.06
Pd, x	7	NH_3, 300; H_2, ---; N_2, 300	27.82
	8	NH_3, 300; H_2, 50; N_2, 250	31.10
	9	NH_3, 300; H_2, 100; N_2, 400	32.15

For pure NH_3 on ruthenium the corresponding plot would be off the diagram to the top right.

TABLE I

AMMONIA DECOMPOSITION *versus* TIME. SUPPORTED Ru CATALYST

NH_3 250 cc.; H_2 250 cc.; N_2 100 cc./min.; Temp., 380°

Time, min.	30	90	150	330	510	660
NH_3 decomposed, %	7.43	7.75	8.12	7.96	8.05	8.15

Effect of Space Velocity.—The rate of ammonia decomposition on ruthenium was observed at three temperatures with pure ammonia at flow rates varying from 200 to 2500 cc. NH_3 per cc. catalyst per hour. In each case a straight line plot, log % NH_3 decomposed *versus* log space velocity was obtained. The decomposition varied with, approximately, the 0.4 power of the space velocity uncorrected for hydrogen formed in the decomposition. Only ruthenium was thus studied.

Effect of Nitrogen.—At a temperature of 380° on the Ru catalyst the percentage decomposition was measured at constant flow rates of ammonia equal to 260 cc./min. and with nitrogen additions varying from 150 to 215 cc./min. The ammonia decomposed in five experiments varied only from 87.0 to 88.8 cc./min. and randomly. Thus, with an exit gas of 172 cc. NH_3/min., 132 cc. H_2/min., and nitrogen varying from 194 to 259 cc./min., without significant variation in rate, it was concluded that nitrogen could be used as a diluent in the subsequent experiments with varying ammonia–hydrogen mixtures.

Effect of Hydrogen.—In one series of experiments on ruthenium, total flow rate and flow rate of ammonia were kept constant while the flow rate of hydrogen was varied. In a second series total flow rate and flow rate of hydrogen were kept constant while the flow rate of ammonia was varied. The range of temperature was from 340 to 400° and chosen so that the maximum decomposition did not exceed 10%. Plots of the log NH_3 decomposed *versus* log (NH_3 for H_2)/(total flow) in each case gave straight lines from which a kinetic expression of the form $-d[NH_3]/dt = k[NH_3]^m[H_2]^n$ can be derived. The exponent m, over the range 360 to 400°, varied between 0.60 and 0.74. The exponent n over the same range varied between -0.91 and -0.95. It will be noted that exponents $m = 0.6$ and $n = -0.9$ would conform to the demands of the Temkin and Pyzhew formulation of the kinetic process.[2]

Effect of Temperature.—Measurements with the ruthenium catalyst in the temperature range 350 to 400° gave linear variations for log (NH_3 decomposed) *versus* $1/T$, with various mixtures of ammonia, hydrogen and nitrogen as shown in Fig. 1. From the linear plots an activation energy of 30.5 ± 0.2 kcal. can be computed for each of three mixtures.

---

(2) M. Temkin and V. Pyzhew, *Acta Physicochim.* (*URSS*), **12**, 327 (1940).

In contrast to the case of ruthenium, a 0.5% palladium catalyst supported on alumina gave decomposition of ammonia in the range of 2 to 10% only in the temperature range of 510 to 570°, with mixtures of ammonia and nitrogen, 300 cc. per minute of each constituent. The activation energy obtained from a log (NH_3 decomposed) *versus* $1/T$ gave a straight line of slope corresponding to an observed activation energy of 27.8 kcal. Experiment shows that this observed increasing activation energy should be corrected for the increasing inhibition by hydrogen as the extent of decomposition increases. This inhibitory influence of hydrogen on the palladium catalyst is very considerable. Thus, with a mixture composed of 300 cc. NH_3 + 100 cc. H_2 + 400 N_2 per min. the decomposition of ammonia on palladium only reached 2% at the temperature of 590°. Even with 300 cc. NH_3, 50 cc. H_2 and 250 cc. N_2 per min. decompositions between 2 and 4% were recorded in the temperature range 580 to 610°. The observed activation energies in these hydrogen-inhibited decompositions are 31.6 ± 0.5 kcal. The data are plotted in Fig. 1.

With rhodium, the data obtained are intermediate between ruthenium and palladium. The temperature range is 360 to 400° for 2 to 10% decomposition of pure ammonia, 400 to 450° for ammonia admixed with nitrogen and hydrogen. The observed activation energies from the log k_1 *vs.* $1/T$ plots in Fig. 1 are *ca.* 30 kcal.

Discussion

The data here recorded are complementary and supplementary to new data of Trapnell[3] on the chemisorption of gases on evaporated metal films. His results show that there is a definite order of affinities of gases common to all metal surfaces studied. The order established is $O_2 > C_2H_2 > C_2H_4 > CO > H_2 > N_2$. Trapnell found that if an evaporated metal chemisorbs a particular gas in the temperature range 0 to −180° it will also chemisorb all gases higher in the scale. If it does not chemisorb a gas it will not chemisorb the gases lower in the scale. The evaporated metal films examined fell into 6 groups, A to F. The metals in Group A which chemisorb nitrogen and hence all the other gases named included W, Ta, Mo, Ti, Zr, Fe, Ca, Ba. Those in Group B which do not chemisorb nitrogen but chemisorb hydrogen and the remaining gases include Ni, Pd, Rh, Pt.

Our data would indicate that ruthenium should be included in Group A while the activity of our palladium catalyst is consonant with Trapnell's assignment of the metal to Group B. Such assignment would make allowance for the usual differences in operating temperatures for reaction on technical catalysts in comparison with the data for chemisorption on metal films.

Our data indicate that ruthenium is more comparable with iron in the one series and with osmium[4] in the other series of the Group VIII metals than it is with palladium. This is a general feature of these triads, the similarity between the corresponding members of the light and heavy triads being more striking than that between the members of the same triad.[5]

The data presented in this paper differ sharply from those of Kiperman,[6] who studied the rate of ammonia synthesis at atmospheric pressure between 550 and 735° on ruthenium catalysts supported on silica gel. He found an activation energy equivalent in the decomposition reaction to one of 59.2 kcal. with evidence of strong inhibition by hydrogen. Our catalysts operating in a temperature range 200–300° lower in temperature are obviously not comparable with the Russian data. We are extending our researches to determine catalytic activity of these metals in other preparations, using both the metals and other supports.

Obedience to the Temkin–Pyzhew kinetics in the case of ruthenium suggests that in this case also, as with iron, the chemisorption of nitrogen in synthesis and desorption in ammonia decomposition is the slow process. With palladium these processes require a higher temperature but a similar observed activation energy. This behavior toward the $N{\equiv}N$ bond is in striking contrast with that found by Kemball[7] in his studies of the NH_3 + D_2 interaction on evaporated metal films. In his work the activation energies of the reaction yielded the sequence: Pt, 5.2; Rh, 6.7; Pd, 8.5; Ni, 9.3; W, 9.2; Fe, 12.5; Cu, 13.4; Ag, 14.1 kcal. From these data it is evident that the breaking of N–H and H–H bonds is most easily achieved on platinum. It is also evident, from the position of iron in the sequence, that the ammonia–deuterium exchange is no guide to the choice of a suitable catalyst for ammonia synthesis or decomposition to its elements. This again is auxiliary evidence of the chemisorption and desorption of nitrogen as the process with a high potential energy barrier to reaction.

The cumulative effect of these data by Trapnell and Kemball and from the present work is to emphasize how sparse is our present knowledge of the chemistry involved in the association between gases and metal surfaces that is involved in chemisorption and catalytic reaction. We concur in and amplify Trapnell's conclusion that high activity is in general associated with transition metals or metals having the characteristic partly filled d band of the transition metals. We amplify the falling activity as a transition period ends by the insertion of ruthenium in the sequence Mo (42), Ru (44), Rh (45), Pd (46), Ag (47), Cd (48), In (49). We concur in his view that there appears to be no general correlation between activity in chemisorption and either surface geometry or work function. We emphasize the chemistry that is paramount in chemisorption of nitrogen by these sequences of metals and call attention to our inability to formulate such chemistry, as yet, in terms of the electronic architecture of the metals.

We are extending these studies on ruthenium, rhodium and palladium to other members of the Group VIII triads, to the exchange reactions between N_2^{14} and N_2^{15} and to the chemisorption of

---

(3) B. M. W. Trapnell, *Proc. Roy. Soc.* (*London*), **A218**, 566 (1953).

(4) W. R. F. Guyer, G. G. Joris and H. S. Taylor, *J. Chem. Phys.*, **9**, 287 (1941).

(5) R. F. Vines, "The Platinum Metals and their Alloys," International Nickel Co., New York, N. Y., 1941, p. 10.

(6) S. Kiperman, *Zhur. Fiz. Khim.*, **21**, 1435 (1947).

(7) C. Kemball, *Proc. Roy. Soc.* (*London*), **A214**, 413 (1952).

methane on these surfaces. It appears from Kemball's researches[8] that methane permits a similar differentiation between metal surfaces and their capacity to chemisorb gases.

Acknowledgment.—This work has been made possible by a generous grant from Baker and Co. to the James Forrestal Research Center at Princeton which is being used for work in catalysis by platinum metals and for studies in the metal science of these elements. Our thanks are due especially to Mr. Chas. W. Engelhard for financial support, and to Dr. E. F. Rosenblatt and to Dr. W. Cohn for assistance in the preparation and provision of catalytic materials. We express our thanks also to Dr. M. Boudart for supervision and criticism of this work.

PRINCETON, N. J.

---

(8) C. Kemball, *Proc. Roy. Soc. (London)*, **A217**, 376 (1953).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Reduced Equation for Viscoelastic Behavior of Amorphous Polymers in the Transition Region[1]

BY A. V. TOBOLSKY AND E. CATSIFF

RECEIVED FEBRUARY 6, 1954

A law of corresponding states is proposed for the viscoelastic properties of amorphous polymers in the transition region. Tables are presented from which the modulus–temperature curve (modulus measured after any fixed time t_1) can be constructed for many polymers.

Introduction

In previous publications,[2,3] it was proposed that the composite stress–relaxation curves of amorphous polymers in the transition region could be adequately reproduced by the equation

$$\frac{\log E_r(t/K) - \frac{1}{2}\log E_1E_2}{\frac{1}{2}\log (E_1/E_2)} = -\operatorname{erf}(h \log t/K) \quad (1)$$

where

$E_r(t/K) = E_{r,T}(t)$ = stress/strain in a sample maintained at a constant small strain for a time t at a temp. T

K = characteristic relaxation time, a function of temp. only for a given polymer

E_1 = quasistatic glassy modulus (usually about $10^{10.5}$ dynes/cm.^{2})

E_2 = quasistatic rubbery modulus (usually between 10^7 and 10^8 dynes/cm.^{2})

h = a parameter characteristic of each polymer

$\operatorname{erf} x = 2\pi^{-1/2}\int_0^x \exp(-x^2)\,dx$, the error integral[4]

Furthermore, it was shown that the temperature dependence of K for the polymers studied to date was

$$h \log K_R = f(T_R)$$

with $f(T_R)$ very nearly the same for all polymers. $f(T_R)$ is tabulated in Table I.

$K_R = K/K_d$

$K_d = K$ at T_d

$T_R = T/T_d$

T_d = distinctive temp. which is related to, if not equal to, the glass transition temp.

TABLE I

REDUCED-TEMPERATURE DEPENDENCE OF $f(T_R)$

T_R	$f(T_R)$	T_R	$f(T_R)$
0.940	1.62	1.000	0.00
.945	1.55	1.005	− .18
.950	1.46	1.010	− .34
.955	1.36	1.015	− .50
.960	1.25	1.020	− .63
.965	1.11	1.025	− .78
.970	0.98	1.030	− .92
.975	.84	1.035	−1.06
.980	.69	1.040	−1.18
.985	.52	1.045	−1.31
.990	.36	1.050	−1.43
.995	.18		

The Reduced Equation of Viscoelastic Behavior.—Just as it is very convenient to express compressibility data of fluids in terms of reduced temperature, pressure and volume, it would also be very desirable to express the viscoelastic properties of amorphous substances in terms of reduced variables. In this case, the most important reduced variable is the reduced temperature $T_R = T/T_d$. Qualitatively, the viscoelastic properties of amorphous polymers (in the transition region) are very similar at the same value of the reduced temperature. It is the purpose of this paper to establish this relation in a quantitative sense.

Equation 1 is essentially a five-parameter reduced equation for viscoelastic behavior of amorphous polymers in the transition region. However, it is not the simplest reduced equation possible. By comparing the values of h and T_d obtained in papers I and II on six amorphous polymers, it becomes clear that $hT_d = 100$ (±3.7) (in °K.). Also $\log K_d = -1.45$ (±0.12) (in hours).

If these values are substituted in equation 1 the following is obtained

$$Y = \frac{\log E_{r,T}(t) - \frac{1}{2}\log E_1E_2}{\frac{1}{2}\log (E_1/E_2)} = -\operatorname{erf}\left[\frac{100}{T_d}(\log t + 1.45) - f(T/T_d)\right] \quad (2)$$

---

(1) Part III of a series on elastoviscous properties of amorphous polymers in the transition region.

(2) J. Bischoff, E. Catsiff and A. V. Tobolsky, THIS JOURNAL, **74**, 3378 (1952), hereinafter called paper I.

(3) E. Catsiff and A. V. Tobolsky, *J. Appl. Phys.*, in press, hereinafter called paper II.

(4) Tables of the error integral may be found in Jahnke and Emde, "Tables of Functions," B. G. Teubner, Leipzig and Berlin, 1933; J. W. Mellor, "Higher Mathematics for Students of Chemistry and Physics," Longmans, Green and Co., London, 1909.