Since α is initially independent of the amount of added CH_4, the first fraction on the right-hand side of equation II can be obtained to a close approximation as the CD_3H/CD_4 ratio in the absence of added CH_4. If the reasonable assumption $k_{1a} \approx k_{1b}$ is made, equation II becomes

$$CD_3H/CD_4 = (CD_3H/CD_4)_0 + (k_3/k_1)(M/[(\text{A-}d_6) + (\text{A-}d_5)]) \quad \text{(III)}$$

where $(CD_3H/CD_4)_0$ is the ratio in the absence of added methane. Thus k_3/k_1 can be obtained from the initial ratio of mass 19/mass 20, $(CD_3H/CD_4)_0$ and a knowledge of the composition of the initial mixture. In the temperature range 350–428° the CD_3H/CD_4 ratio was dependent upon the time of photolysis for methane:acetone-d_6 mixtures. Since this ratio was found to be almost linear with time, a short extrapolation to zero time was applied to the ratio after correction for $(CD_3H/CD_4)_0$. This gave $(k_3/k_1)(M/[(\text{A-}d_6) + (\text{A-}d_5)])$. In contrast to the photolysis, the $M/[(\text{A-}d_6) + (\text{A-}d_5)]$ ratio did not change appreciably in the course of pyrolysis, so that it was not necessary to extrapolate to zero time. The constancy of this ratio was reflected in the constancy with time of the CD_3H/CD_4 ratio in the pyrolyses. In the case of the photolyses, the smaller percentage of methane in the products made it necessary to carry out the reactions to greater percentage conversions of deuterioacetone in order to obtain enough products for analysis. Hence extrapolation of CD_3H/CD_4 to zero time was necessary in the photolyses. The line drawn through the points in Fig. 1 was drawn by the method of least squares. Since

$$k_3/k_1 = (A_3/A_1)e^{(E_1-E_3)/RT} \quad \text{(IV)}$$

where A_3 and A_1 are the Arrhenius pre-exponential factors for reactions 3 and 1, respectively, a plot of log k_3/k_1 *vs.* $1/T$ should give a straight line of slope $(E_1 - E_3)/4.576$ and intercept log A_3/A_1. Using this treatment and applying the method of least squares, $E_3 - E_1 = 2.74$ kcal./mole and $A_3/A_1 = 0.48$. It has been shown[4,5] that $E_1 = 11.3$ kcal./mole, and therefore $E_3 = 14.0$ kcal./mole. These activation energies are based upon an energy of activation of 9.6 kcal./mole for the abstraction of H from acetone by CD_3 and an activation energy of zero for the methyl–methyl combination. Since CH_3 and CD_3 have previously been shown[5] to take a hydrogen atom from normal acetone with equal facility, it is reasonable that CD_3 and CH_3 abstract a hydrogen atom from methane with equal facility.

Figure 1 demonstrates that it is entirely practical to study reactions of methyl radicals using both photochemical and pyrolytic techniques concurrently. In addition to giving results in harmony with photolysis, the pyrolytic technique can be used, as it has been here, to establish the presence or absence of hot radicals. In the present case it is evident that hot radicals cannot be present in the photolysis since they are absent in the pyrolysis and the two techniques give consistent results.

Table II and Fig. 1 show clearly that the reaction of CD_3 radicals with CH_4 is partly heterogeneous relative to the reaction of CD_3 with CD_3COCD_3. A sixfold increase in the surface area caused a ten per cent. increase in the ratio k_3/k_1. If the reaction of CD_3 with acetone-d_6 is homogeneous, it may be concluded that the rate of the homogeneous reaction between CD_3 and methane is at least 98% of the observed rate. Therefore, if the CD_3–acetone-d_6 reaction is homogeneous, the data obtained without added surface represent the homogeneous reaction of CD_3 with methane within the limits of experimental error. If homogeneity of acetone decomposition were established beyond any doubt, the relative heterogeneity of methyl radical reactions could be studied conveniently and quantitatively using the technique outlined here.

Acknowledgment.—The authors wish to thank Dr. S. Ruven Smith and Mr. William Golyer for the mass spectrometric analyses.

[5] J. R. McNesby and Alvin S. Gordon, THIS JOURNAL, **76**, 1416 (1954).

INYOKERN, CHINA LAKE, CALIF.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

γ-Ray-Induced Oxidation of Aqueous Formic Acid–Oxygen Solutions. Effect of *p*H

BY EDWIN J. HART

RECEIVED MARCH 29, 1954

Radiation yields of carbon dioxide, hydrogen and hydrogen peroxide formed and oxygen reacted have been measured at 0.01 *M* formic acid concentration over the *p*H range from 0.32 to 11.58. In the *p*H range above 3, molecular hydrogen and hydrogen peroxide are formed in equimolar amounts. Below this range of *p*H, an excess of hydrogen peroxide is formed. The results are interpreted in terms of number of water molecules dissociated in three primary reactions: (1) $H_2O = H + OH$, (2) $H_2O = {}^1/_2H_2O_2 + {}^1/_2H_2$, and (3) $H_2O = H + {}^1/_2H_2O_2$. Each of these three reactions is *p*H dependent. However, the total number of water molecules decomposed/100 e.v. is substantially constant in the *p*H range 0.32 to 11.58 and equals 3.99 ± 0.14.

The formic acid–oxygen system has been employed to measure the radical pair and molecular product yields of ionizing radiations in aqueous solutions.[1] Specifically, the yield of oxygen consumption, $G_{(-O_2)}$, provides a measure of free radicals available, whereas the yield of hydrogen extrapolated to infinite oxygen concentration, $G_{(H_2)}$, is a measure of reaction 2.

$$H_2O = H + OH \quad (1)$$

$$H_2O = {}^1/_2H_2 + {}^1/_2H_2O_2 \quad (2)$$

Recently Allen[2] has been led to postulate a third

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[1] (a) E. J. Hart, *J. Phys. Chem.*, **56**, 594 (1952); (b) THIS JOURNAL, **76**, Sept. (1954); (c) *Rad. Research*, **1**, 53 (1954).

[2] A. O. Allen, Brookhaven National Laboratory report BNL-1498 (1953); *Rad. Research*, **1**, 85 (1954).

primary reaction in order to explain the excess yield of hydrogen peroxide over hydrogen reported

$$H_2O = H + {}^1/_2H_2O_2 \qquad (3)$$

by Dainton and Sutton[3] in the oxidation of ferrous sulfate at low concentrations. No indication of reaction 3 was shown by the formic acid work carried out at *p*H 2.7. Since the ferrous sulfate results were obtained in 0.8 *N* sulfuric acid at *p*H 0.5, an influence of *p*H on the yield of reaction 3 could explain the difference between the formic acid and ferrous sulfate results. In the present work the effect of *p*H on the yields of free radical and molecular products in reactions 1, 2 and 3 are reported for aqueous formic acid–oxygen solutions.

Experimental

Irradiations were carried out using radioactive cobalt at dosage rates of 0.053 × 10^{20} and 2.03 × 10^{20} e.v./l. min. Dosage rates were measured by means of the ferrous sulfate dosimeter and the Hochanadel–Ghormley value of G = 15.5 ferric ions/100 e.v. of energy.[4]

Experimental techniques are similar to those described in earlier papers.[1] Reagent grade sulfuric acid, sodium hydroxide and sodium formate were used in the preparation of the solutions. Hydrogen peroxide was measured spectrophotometrically by absorption of the triiodide ion at 3500 Å. using the Ghormley method previously outlined.[5] A constant factor of 38.4 instead of 40.0 was used to calculate the hydrogen peroxide concentration from the optical density.

Performic acid was prepared following the method used by Greenspan.[6] Approximately 50% of total peroxide was present as performic acid in solutions prepared by reacting 2.3 g. of formic acid, 2.8 g. of 90% hydrogen peroxide and 0.04 g. of sulfuric acid at 0° for 30 minutes. On dilution in 1.0 *N* sulfuric acid, hydrolysis proceeded slowly over a period of several hours. The rate of hydrolysis depends on the concentration of peroxide. It was found that the hydrogen peroxide concentration can be determined by rapid titration with ceric sulfate whereas the total peroxide content can be measured by the triiodide ion method referred to above. However, neither of these methods is suited to the determination of micromolar quantities of performic acid in aqueous solutions. The following method was employed to test irradiated formic acid–oxygen solutions for performic acid: A preliminary experiment showed that hydrogen peroxide could be measured spectrophotometrically quickly and accurately in formic acid solutions by ceric ion absorption at 3300 Å. Performic acid solutions added to ceric sulfate showed a dependence on time of standing. The change is presumably due to hydrolysis of performic acid into hydrogen peroxide and formic acid. In a sample of performic acid having a final peroxide content of 93 μM hydrogen peroxide, 71 μM hydrogen peroxide was found initially. Under the condition of this test, with an original 198 μN Ce^{+4} solution in 1.0 *N* sulfuric acid, 10 minutes were required for completion of the hydrolysis. It is concluded that 22 μM performic acid was present upon addition of the ceric sulfate solution.

Results and Discussion

The effect of *p*H on the yields of carbon dioxide, hydrogen and hydrogen peroxide production and oxygen consumption was studied at dosage rates of 2.03 × 10^{20} and 5.26 × 10^{18} e.v./l. min. (see Table I and Fig. 1). In both cases initial slopes were obtained from dosage curves.

TABLE I

INITIAL YIELD OF PRODUCTS IN THE GAMMA-RAY OXIDATION OF AQUEOUS 0.01 *M* FORMIC ACID

Exp. no.	*p*H	Dosage rate, e.v./l. min. × 10^{-20}	O_2, m*M*	$G_{(CO_2)}$	$G_{(-O_2)}$	$G_{(H_2)}$	$G_{(H_2O_2)}$	$G_{(3)}$
1	0.32	2.03	0.388	2.50	3.20	0.38	3.72	0.84
2	1.28	2.03	.417	2.59	3.15	.42	3.82	.81
3	2.75	2.03	.441	2.76	2.86	.58	3.36	.02
4	6.81	2.03	.399	2.96	2.83	.53	3.46	− .03
5	11.58	2.03	.438	3.04	3.02	.56	3.52	− .08
6	0.32	0.0526	1.03	2.53	2.81	.37	4.08	1.18
7	1.28	.0526	1.12	2.51	2.81	.43	3.95	1.01
8	2.10	.0526	1.12	2.61	3.09	.40	3.68	0.67
9	2.70	.0526	1.13	3.08	3.01	.42	3.54	.04
10	3.72	.0526	1.18	3.18	3.29	.45	3.52	− .11
11	4.92	.0526	1.17	3.28	3.02	.45	3.80	.07
12	6.81	.0526	1.18	2.90	2.90	.46	3.60	.24
13	11.20	.0526	1.25	3.02	3.02	.46	3.48	.00

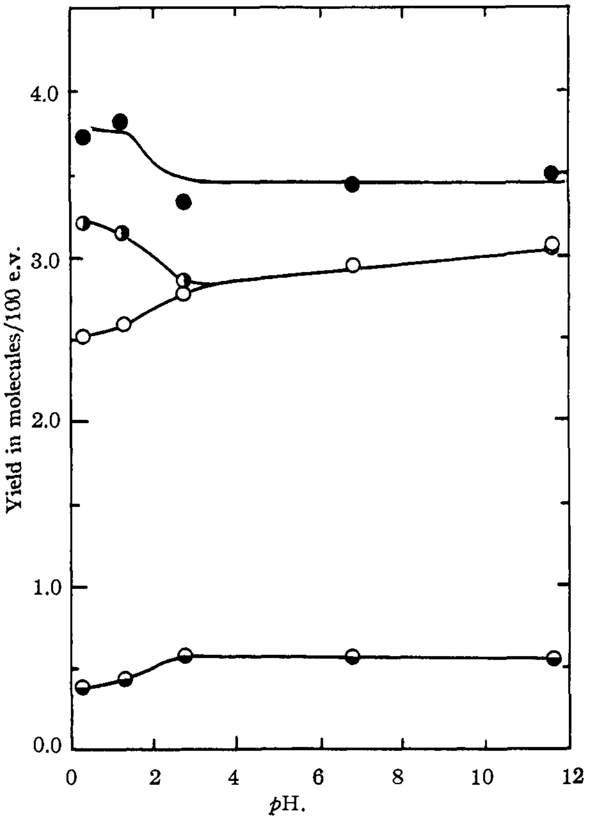

Fig. 1.—Effect of *p*H on the γ-ray-induced oxidation of aqueous 0.01 *M* formic acid plus 0.416 m*M* O_2 at a dosage rate of 2.03 × 10^{20} e.v./l. min.: ●, H_2O_2; ◑, $-O_2$; ○, CO_2; ⊖, H_2.

In the range of *p*H from 2.7 to 11.6 (exp. no. 3–5 and 9–13) product formation is independent of *p*H. However, in the acid range below a *p*H of 2.7 hydrogen peroxide formation and oxygen consumption in exp. 1 and 2 rise perceptibly above the averages for the higher *p*H's. Carbon dioxide and hydrogen production, however, fall in acid solutions. The accuracy of the data is greater in exp. 1–5 than in 6–13 since the former experiments were carried out at lower oxygen concentrations. Small differences in gas formation and consumption can be measured with greater precision at lower total concentrations of oxygen.

By setting up a mechanism similar to the one employed previously[1b] but lacking the formate

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[3] F. S. Dainton and H. C. Sutton, *Discs. Faraday Soc.*, No. 12, 121 (1952); *Trans. Faraday Soc.*, **49**, 1101 (1953).

[4] C. J. Hochanadel and J. A. Ghormley, *J. Chem. Phys.*, **21**, 880 (1953).

[5] E. J. Hart, THIS JOURNAL, **73**, 68 (1951).

[6] F. P. Greenspan, *ibid.*, **68**, 907 (1946).

radical–hydrogen peroxide step and including reaction 3, one is able to estimate the contribution of each of the primary steps postulated. In addition to reactions 1–3 we have

$$OH + HCOOH = H_2O + HCOO \quad (4)$$
$$H + HCOOH = H_2 + HCOO \quad (5)$$
$$HCOO + O_2 = HO_2 + CO_2 \quad (6)$$
$$H + O_2 = HO_2 \quad (7)$$
$$HO_2 + HO_2 = H_2O_2 + O_2 \quad (8)$$

One derives the following equations by assuming that steady-state concentrations of intermediate hydrogen, hydroxyl, formate and hydroperoxy free radicals are quickly established

$$G_{(H_2O_2)} = G_{(1)} + G_{(2)}/2 + G_{(3)} \quad (9)$$
$$G_{(-O_2)} = G_{(1)} + G_{(3)}/2 \quad (10)$$
$$G_{(H_2)} = G_{(2)}/2 + \frac{G_{(1)} + G_{(3)}}{1 + k_7(O_2)/k_5(HCOOH)} \quad (11)$$
$$G_{(CO_2)} = G_{(1)} + \frac{G_{(1)} + G_{(3)}}{1 + k_7(O_2)/k_5(HCOOH)} \quad (12)$$

The experimental results of Table I provide the data necessary for the calculation of $G_{(1)}$, $G_{(2)}$ and $G_{(3)}$ from these equations, giving the yield of water molecules dissociated/100 e.v. in reactions 1, 2 and 3, respectively. Under the experimental conditions used k_7/k_5 equals 530.[1b] At oxygen and formic acid concentrations of 0.001 and 0.01 *M*, respectively, $G_{(2)}/2 = G_{(H_2)}$ and $G_{(1)} = G_{(CO_2)}$ to a first approximation. A preliminary value for $G_{(3)}$ may then be calculated from eq. 9 (see column 9 of Table I). Within the limits of experimental error, $G_{(3)}$ approaches zero at *p*H's of about 3.0 and higher. By inserting these approximate values in eq. 11 and 12, corrected values are calculated for $G_{(1)}$ and $G_{(2)}$. Equations 9 and 10 may then be used to determine $G_{(3)}$. These adjusted values are given in Table II, and the averages are plotted in Fig. 2.

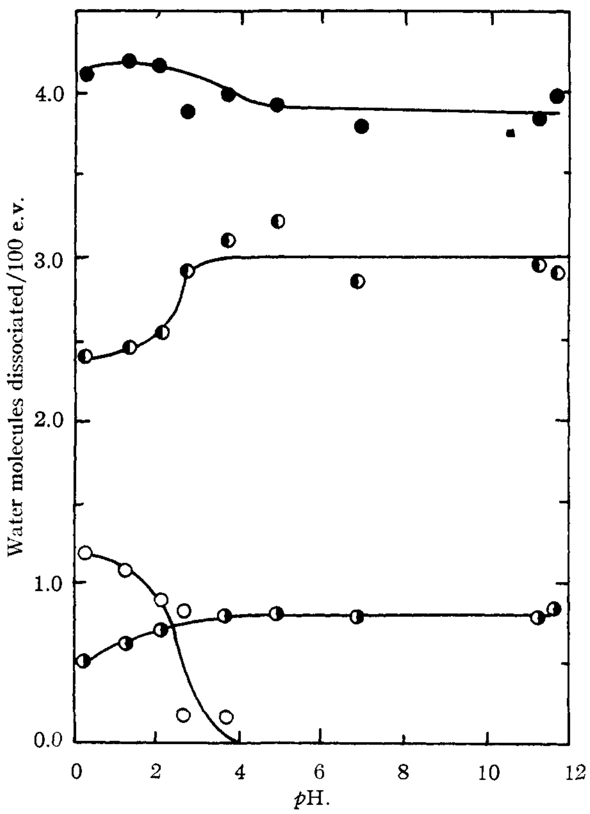

Fig. 2.—Effect of *p*H on the primary dissociation of water in 0.01 *M* formic acid by Co^{60} γ-rays: ●, G_{Tot}; ◐, $G_{(1)}$; ◑, $G_{(2)}$; ○, $G_{(3)}$.

TABLE II

EFFECT OF *p*H ON PRIMARY REACTIONS

*p*H	$G_{(1)}$	$G_{(2)}$	$G_{(3)Av}$	G_{Tot}
0.32	2.40	0.53	1.19	4.12
1.28	2.44	.64	1.09	4.17
2.10	2.56	.70	0.91	4.17
2.70	2.83	.84	.19	3.86
3.72	3.13	.80	.16	3.99
4.92	3.23	.80	− .10	3.93
6.81	2.84	.82	.14	3.80
11.20	2.97	.82	.08	3.87
11.58	2.92	.88	.18	3.98

There is a slight indication that the total number of water molecules dissociated at *p*H's less than 3 is greater than at higher *p*H's. However, the average value for all *p*H's is 3.99 ± 0.14. The significant changes in $G_{(1)}$, $G_{(2)}$ and $G_{(3)}$ occur at *p*H's less than 3 (see Fig. 2). $G_{(3)}$ appears to arise at the expense of $G_{(1)}$ and $G_{(2)}$ and drops to one half its acid value at a *p*H of 2.5.

The experimental results at low *p*H could theoretically be explained by the assumption that performic acid is a product of the free radical-induced reaction. In case performic acid were stable in acid solutions and present to the extent of 25% of the total peroxide, it would be unnecessary to assume reaction 3 at low *p*H. Performic acid reacts as hydrogen peroxide in the triiodide test thereby providing the full yield of peroxide but essentially ties up carbon dioxide which is produced through the action of hydrogen and hydroxyl radicals as shown by reactions 4, 5 and 6. Hydrogen atoms from reaction 3 operating largely *via* reaction 7 and 8 produce hydrogen peroxide and no carbon dioxide. Therefore to the extent that performic acid is found, the hydrogen and hydroxyl radicals produced in reaction 1 behave like the hydrogen atom in reaction 3, each reaction leading only to the formation of peroxide. For this reason it is important to demonstrate the presence or absence of performic acid in the irradiated solutions in order to support the hypothesis that reaction 3 exists.

A comparison of the behavior of performic acid toward ceric sulfate with that of a two-minute γ-ray irradiation of formic acid–oxygen solution of *p*H 0.32 has been made. Two hundred micromolar ceric sulfate is instantly reduced by the irradiated solution and but slowly reduced by performic acid in concentrations of the order of 20 μM. (For details see the Experimental section.) Thus it is concluded that performic acid is not a product of the γ-ray irradiations at *p*H 0.32 and that the assumption of reaction 3 or its equivalent is substantiated by these data.

Dainton and Sutton treat their experimental data in a different but essentially equivalent manner. These authors assume that neither the molecular 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.

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(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

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