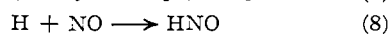
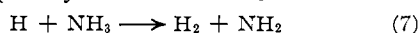
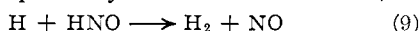


Reaction 5 has been suggested<sup>2</sup> as a branching step in NO-NH<sub>3</sub> flames. Whether eq. 5 results in chain branching will probably depend on whether H atoms subsequently react with NH<sub>3</sub> or with NO.



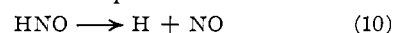
Since NO is known to "catalyze" the recombination of H atoms,<sup>13</sup> probably *via* reactions 8 and 9, it is



conceivable that only the H atoms which undergo reaction 7 will function as chain carriers.

(13) H. M. Smallwood, *THIS JOURNAL*, **51**, 1985 (1929).

If the activation energy of  $k_2$  is associated with the chain branching step, the observed value of 30 kcal. is too large to be attributed to reaction 7. Alternatively, the decomposition of HNO



might require such an energy of activation and reaction 10, followed by reaction 7, would result in branching.

Although this admittedly speculative mechanism predicts temperature and composition dependent explosion limits the complex form of the resulting rate expression makes comparison with eq. 1 rather futile.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF THE UNIVERSITY OF QUEENSLAND, AUSTRALIA, AND THE UNIVERSITY OF BUFFALO, BUFFALO, NEW YORK]

## The Oxidation of Thiocyanate Ion by Hydrogen Peroxide. II. The Acid-catalyzed Reaction

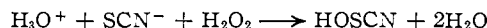
By I. R. WILSON AND G. M. HARRIS

RECEIVED JULY 19, 1960

The stoichiometry and kinetics of the acid-catalyzed reaction have been studied in the range 0.05 to 1.3 *M* perchloric acid. The main products are sulfate and hydrogen cyanide, but sulfur dicyanide, S(CN)<sub>2</sub>, is also formed. The reaction, as determined by iodometry, follows a rate law of the form

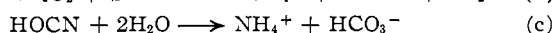
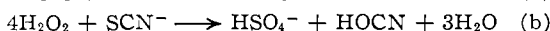
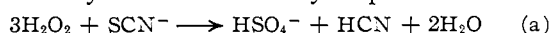
$$R = k_2(\text{H}^+)(\text{SCN}^-)(\text{H}_2\text{O}_2)^2/[(\text{H}_2\text{O}_2) + \alpha(\text{HCN})]$$

in which  $\alpha$  is a constant. A mechanism of reaction is deduced, making use of carbon-14 and oxygen-18 tracer experiments as well as conventional rate data, and  $\alpha$  is identified as a ratio of rate constants of secondary reactions. The rate constant of the third order primary reaction



is fitted by the expression  $k_2 = 1.75 \times 10^8 \exp(-11000/RT)$  l.<sup>2</sup> mole<sup>-2</sup> min.<sup>-1</sup> in the range 20 to 50°.

In Part I of the present series,<sup>1</sup> it was pointed out that the reaction between hydrogen peroxide and thiocyanate takes place according to different mechanisms, depending on the acidity of the solution. The main acid-catalyzed process is stated to have the stoichiometry<sup>2</sup> of equation a, while the non-catalyzed reaction<sup>1</sup> obeys equations b and c



A re-investigation of the acid-catalyzed reaction is reported herewith, in which alternative rate-measuring methods and isotopic tracer technique have provided conclusive evidence concerning its mechanism.

### Experimental

All reagents used were as specified in the earlier publication.<sup>1</sup> *Stoichiometric and/or rate measurements* were made by several different procedures, including:

(A) Iodometry of H<sub>2</sub>O<sub>2</sub> consumed, as detailed previously.<sup>1</sup> It was found that sulfur dicyanide also liberates I<sub>2</sub> from iodide, so that this determination gives in fact total of (H<sub>2</sub>O<sub>2</sub>) and (S(CN)<sub>2</sub>) in presence of the latter.

(B) Volumetric determination of sulfate formed, using a modification of the EDTA method of Belcher, *et al.*<sup>3</sup> Aliquots of reaction solution were pipetted into 15 ml. centrifuge tubes containing 5 ml. of 0.02*M* BaCl<sub>2</sub> and 1 ml. of acetate buffer (the latter raises the *pH* sufficiently to

"freeze" the reaction). After thorough mixing, centrifuging and washing, the BaSO<sub>4</sub> precipitate was taken up in a mixture of 5 ml. of 0.02 *M* EDTA and 0.5 ml. of concentrated ammonia, while kept at 50–60° on a water-bath. The resulting solution, buffered to *pH* 10 with ammonia/ammonium perchlorate, was titrated with 0.005 *M* Mg-(NO<sub>3</sub>)<sub>2</sub> solution, using as indicator eriochrome black T screened with methyl yellow.

(C) Acidimetric measurement of bisulfate formed, which was possible when the initial concentration of HClO<sub>4</sub> did not exceed 0.1 *M* and the initial thiocyanate concentration was at least 0.01 *M*. Mixed brom cresol green/methyl red indicator was used.

(D) Colorimetric determination of H<sub>2</sub>O<sub>2</sub> consumed using the specific Ti(IV) technique devised by Rynasiewicz.<sup>4</sup> Sulfur dicyanide does not interfere in this determination, as it does in Method A.

(E) Titration of HCN formed during reaction with NiSO<sub>4</sub> using dimethyl glyoxime as indicator,<sup>5</sup> or, in the case of complete reaction, by means of Archer's modification<sup>6</sup> of the Liebig method.

(F) Polarographic determination of thiocyanate consumption.<sup>7</sup>

The *identification of sulfur dicyanide*, S(CN)<sub>2</sub>, in the reaction products was accomplished by ether extraction followed by evaporation of the ether at reduced pressure and two sublimations of the residue at 30°. White crystals were obtained; m.p. 62.0–62.6°. A comparison sample of S(CN)<sub>2</sub> prepared by the reaction of AgSCN and ICN<sup>8</sup> and purified in the same way as the reaction residue gave m.p. 62.0–62.8° and mixed m.p. 61.9–62.8°. The identity of the two products was also confirmed by infrared spectra in CS<sub>2</sub> solution.

(4) J. Rynasiewicz, *Anal. Chem.*, **26**, 355 (1954).

(5) L. G. Urusovskaya and P. I. Zhilina, *C. A.*, **44**, 481 (1950).

(6) E. E. Archer, *Analyst*, **83**, 571 (1958).

(7) R. A. Plowman and I. R. Wilson, *Analyst*, **35**, 222 (1960).

(8) *Beilstein*, III, 180.

(1) I. R. Wilson and G. M. Harris, *THIS JOURNAL*, **82**, 4515 (1960).  
 (2) J. H. Kastle and C. R. Smith, *Amer. Chem. J.*, **32**, 376 (1904).  
 (3) R. Belcher, R. L. Bhasin, R. A. Shah and T. S. West, *J. Chem. Soc.*, 4054 (1958).

A carbon-14-tracer experiment involved reacting a solution 0.06 M in  $H_2O_2$ , 0.02 M in KSCN and 0.1 M in  $HClO_4$  in presence of 0.02 M carbon-14-labelled KCN. Samples were taken at suitable intervals during the early stages of reaction and run through an IRA-400 anion exchange column in the nitrate form. Cyanide passed through readily at this acidity, while the thiocyanate was eluted later with 0.1 N NaOH. AgSCN and AgCN were precipitated separately and assayed for carbon-14 by standard procedure.<sup>9</sup> All the radio-activity remained in the cyanide. Thus the mechanism can include no reaction or series of reactions which enables equilibration of thiocyanate and cyanide carbon, as was also essentially true for the uncatalyzed process.<sup>1</sup>

An oxygen-18 tracer experiment consisted of determining the oxygen isotopic composition of sulfate formed when the peroxide/thiocyanate reaction was run in oxygen-18 enriched water. The sulfate was precipitated from a completely reacted mixture with  $BaCl_2$  and the sulfate oxygen converted to  $CO_2$  for mass spectrometric analysis according to proven procedure.<sup>10</sup> The data showed that approximately 2 atoms of oxygen per sulfate radical were derived from solvent water.<sup>11</sup> This is precisely the result obtained by Halperin and Taube<sup>10</sup> for peroxide oxidation of sulfite to sulfate. Since exchange of sulfate oxygen with water is exceedingly slow under our reaction conditions,<sup>12</sup> it is highly probable that sulfite is a reaction intermediate in the peroxide/thiocyanate reaction.

A test for a free radical mechanism was made by reaction of two solutions of equal  $HClO_4$  and  $H_2O_2$  concentration, but only one of which contained KSCN, in the presence of ultraviolet light from a mercury arc. The peroxide decreases in these solutions were compared with one another and with decreases in identical solutions kept in the dark. No acceleration in the  $H_2O_2/SCN^-$  reaction occurred in the irradiated solution, ruling out any significant contribution of OH radicals to the process. A further test involved carrying out the reaction in presence of acrylonitrile and of an equimolar acrylonitrile-styrene mixture. Polymer was formed in both cases but could have resulted from anionic as well as free radical initiation.<sup>13</sup> The anionic conception is supported by preliminary tests<sup>14</sup> which showed that no styrene was incorporated in the polymer obtained from the mixed monomer experiment.<sup>15</sup>

The effect of trace contaminants was briefly studied. First, it was shown that aged acidic solutions of thiocyanate (which develop a faint  $H_2S$  odor) react at exactly the same rate as fresh solutions. Furthermore, addition of traces of  $NiSO_4$ ,  $Rh(ClO_4)_3$  and  $FeSO_4$  had no effect on the rate, though larger concentration ( $>10^{-6}M$ ) of the ferrous salt caused some acceleration. None of these metal ions were present as contaminants in normal experiments.

### Results and Discussion

Preliminary experiments showed that changes in ionic strength in the range  $0.1 < \mu < 0.6$  made by addition of  $NaClO_4$  had no significant effect on the rate of reaction. No attempt was made, therefore, to adjust ionic strength in subsequent work. Third-order rate constants were calculated from initial concentrations and initial rates according to the expression

$$R_0 = -\frac{1}{3} \left[ \frac{d(H_2O_2)}{dt} \right]_0 = - \left[ \frac{d(SCN^-)}{dt} \right]_0 = + \left[ \frac{d(SO_4)}{dt} \right]_0 = k_0(H^+)_0 (SCN^-)_0 (H_2O_2)_0$$

$k_0$  was satisfactorily constant over a wide range of reactant concentrations irrespective of the rate-

(9) G. M. Harris and F. E. Jenkins, *THIS JOURNAL*, **79**, 276 (1957).

(10) J. Halperin and H. Taube, *ibid.*, **74**, 375 (1952).

(11) We are indebted to Drs. A. N. Bourns and J. Stothers of McMaster University, Hamilton, Ontario, for the oxygen-18 determinations.

(12) T. C. Hoering and J. W. Kennedy, *THIS JOURNAL*, **79**, 56 (1957).

(13) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 224.

(14) L. O'Hara and I. R. Wilson, unpublished work.

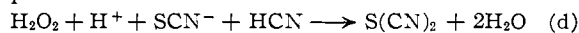
(15) C. Walling, E. R. Briggs, W. Cummings and F. R. Mayo, *THIS JOURNAL*, **72**, 48 (1950).

measuring method used. At 29.9°, a value of  $k_0 = 2.0 \pm 0.3 \text{ l.}^2 \text{ mole}^{-2} \text{ min.}^{-1}$  was obtained in a series of runs in which  $(HClO_4)_0$  was varied between 0.05 and 1.3 M,  $(H_2O_2)_0$  between  $2.5 \times 10^{-2}$  and  $6 \times 10^{-2} M$  and  $(KSCN)_0$  between  $1.0 \times 10^{-2}$  and  $2.5 \times 10^{-2}$ . Results obtained similarly at other temperatures showed that  $k_0$  is 1.1 and  $6.5 \text{ l.}^2 \text{ mole}^{-2} \text{ min.}^{-1}$  at 19.9 and 49.9°, respectively. The corresponding Arrhenius relationship for the temperature range specified is  $k_0 = 1.75 \times 10^8 \exp(-11000/RT) \text{ l.}^2 \text{ mole}^{-2} \text{ min.}^{-1}$ .

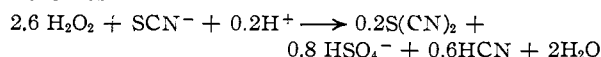
At later reaction times, the rates deviated from the third order law. To illustrate this,  $k_t t$  values were obtained from the slopes of the smooth experimental plots of  $\Delta C$  vs.  $t$ , where  $\Delta C = \frac{1}{3} |\Delta(H_2O_2)|$ ,  $|\Delta(SCN^-)|$  or  $|\Delta(SO_4)|$ . The relationship is

$$k_t t = (d\Delta C/dt)_t / (H^+)_t (SCN^-)_t (H_2O_2)_t$$

It was found that the  $k_t t$  vs.  $t$  curves were exactly linear during the first 15–20 minutes of reaction but thereafter curved off well below the extrapolated straight line. The magnitude of this deviation was greatest for the  $\Delta(SO_4)$  data and least for the  $\Delta(SCN^-)$  data. It is evident that early in the reaction complications set in, which change the rate law and the simple stoichiometry of equation a. Of other possible reaction products sought, only  $S(CN)_2$  was unequivocally identified (see Experimental). A reasonable stoichiometry for this product is

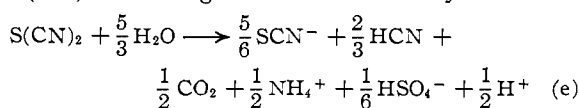


This reaction, as an important adjunct to (a), can account qualitatively for the data. Thus, with a 20% contribution to the total stoichiometry from (d) and 80% from (a), the over-all reaction becomes



so that  $|\Delta(SCN^-)| > |\Delta^{1/3}(H_2O_2 + S(CN)_2)| > |\Delta(HSO_4^-)|$  at later reaction times as suggested by the  $k_t t$  vs.  $t$  data.

More quantitative evidence concerning the formation and fate of the  $S(CN)_2$  was sought in a group of experiments over long reaction times. The sulfur dicyanide concentrations were estimated by taking the difference between the iodometric  $\Delta(H_2O_2)$  (Method A) and the colorimetric  $\Delta(H_2O_2)$  (Method D), with results noted in Table I. Immediate appreciable production of  $S(CN)_2$  is observed only with added HCN, there being a definite period of inhibition in absence of the latter (experiment 1). Also, the maximum in the  $S(CN)_2$  concentration is approximately halved when  $(SCN^-)_0$  is halved (expts. 3 and 4), but  $(S(CN)_2)_{\max}$  is more or less independent of  $(H_2O_2)_0$  (expts. 2 and 3). Finally, when  $(SCN^-)_0$  is considerably in excess (expt. 3), resulting in more rapid and complete disappearance of  $H_2O_2$ ,  $S(CN)_2$  falls off more steeply than otherwise. This fall-off is ascribed to the known acid hydrolysis of  $S(CN)_2$  according to the stoichiometry<sup>16</sup>:



(16) R. H. Smith and I. R. Wilson, unpublished work.

TABLE I  
 S(CN)<sub>2</sub> FORMATION AND DECAY AT 30° IN 0.1 M HClO<sub>4</sub>

Initial concn. (M × 10 <sup>3</sup> )			HCN	(S(CN) <sub>2</sub> ) (M × 10 <sup>2</sup> )	Time (hr.)							
H <sub>2</sub> O <sub>2</sub>	KSCN				1	5	17	27	42	65	92	167
5.86	2.0	0.0		0.04	0.41	0.37	0.43	0.46	0.37	0.29	0.25	
5.86	2.0	2.0		.35	.73	.90	.82	.81	.71	.64	.37	
2.94	2.0	2.0		.25	.73	.91	.84	.57	.43	.25	...	
5.86	1.0	2.0		.29	.39	.34	.39	.31	.22	.27	.24	

The half-time of reaction e is estimated from the data of experiment 3 (for times >27 hr.) at ca. 40 hr., in fair agreement with an estimate of about 50 hr. from data on pure S(CN)<sub>2</sub> hydrolysis under similar conditions.<sup>16</sup>

The effect of HCN was further investigated by making a more complete analysis of the stoichiometry in reaction mixtures which had stood long enough for all H<sub>2</sub>O<sub>2</sub> to be consumed, with the results shown in Table II. High initial (HCN)

 TABLE II  
 STOICHIOMETRY OF REACTION IN 0.1 M HClO<sub>4</sub> AT 30° IN PRESENCE OF ADDED HCN

Initial Conc. (M × 10 <sup>3</sup> )			Final Conc. (M × 10 <sup>3</sup> )		
H <sub>2</sub> O <sub>2</sub>	KSCN	HCN	HCN	HSO <sub>4</sub> (obsd.)	HSO <sub>4</sub> (calcd.)
5.82	5.01	0.00	1.25	1.74	1.77
5.93	2.07	1.00	1.33	1.54	1.56
5.93	2.07	2.00	1.74	1.40	1.42

is seen to lead to net consumption of the latter, pointing to the considerable significance of reactions d and e under such circumstances. Confirmation of the suggested stoichiometry of reactions a, d and e is provided by the figures on sulfate concentration. The reactions require that  $|\Delta(\text{H-SO}_4)| = \frac{1}{4} [\Delta(\text{H}_2\text{O}_2) + \Delta(\text{HCN})]$ , and the last columns of the Table show how satisfactorily this requirement is obeyed.

Reaction d suggests that the initial reaction rates with added HCN should differ from those obtained otherwise. To test this, experiments were done at two temperatures utilizing iodometric measurements (Method A). The results are in Table III. There is a pronounced decrease in the

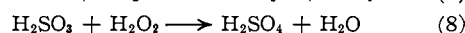
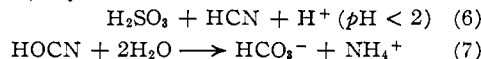
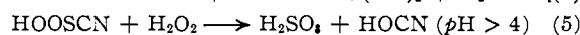
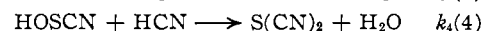
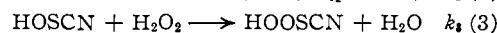
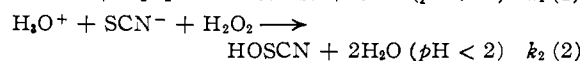
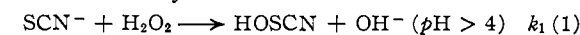
 TABLE III  
 INITIAL RATE OF REACTION IN 0.1 M HClO<sub>4</sub> IN PRESENCE OF HCN

Initial concn. (M × 10 <sup>2</sup> )			Rate constant (l. <sup>2</sup> mole <sup>-2</sup> min. <sup>-1</sup> )	
H <sub>2</sub> O <sub>2</sub>	KSCN	HCN	k <sub>0</sub>	k <sub>2</sub>
A. Results at 19.9°				
5.72	1.99	0.00	1.3	1.3
5.72	1.99	0.97	1.0	1.3
5.72	1.99	1.93	0.8	1.3
1.14	1.99	1.93	.3	1.3
5.72	0.40	1.93	.8	1.3
B. Results at 29.8°				
3.80	1.33	0.00	2.3	2.3
3.69	1.33	.10	2.1	2.2
3.69	1.33	.19	2.0	2.2
6.29	1.33	.38	1.8	2.0
3.70	1.33	.76	1.65	2.3

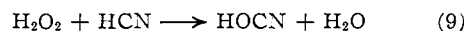
simple initial third order rate constant  $k_0$  in presence of added HCN. However, use of the expression  $R_0 = k_2(\text{H}^+)_0(\text{SCN}^-)_0(\text{H}_2\text{O}_2)_0^2/[(\text{H}_2\text{O}_2)_0 + \alpha(\text{HCN})_0]$  (f) leads to an excellently invariant rate constant

$k_2$ , with the parameter  $\alpha$  set equal to 2.0 at both temperatures. It is seen that (f) reduces to the simple third order law when  $(\text{HCN})_0 = 0$ , in which case  $k_0 \equiv k_2$ .

A comprehensive mechanism which fulfills the requirements of our data on both non-catalyzed<sup>1</sup> and acid-catalyzed reactions is



Reactions 1, 3, 5, 7 and 8, with (1) rate-determining, account for the kinetics and stoichiometry of the non-catalyzed reaction in every respect except one. This is the appearance of a small amount of cyanide carbon in the carbonate product in experiments with added labelled cyanide. This must be due to a contribution from the known measurable, if slow, reaction<sup>17</sup> in neutral or slightly basic solution:



followed by (7). In strongly acid solution, reaction 9 is very slow<sup>17</sup> so there is no interference in the carbon-14 tracer experiment at low pH in the early stages of reaction. The species HOSCN is proposed for the product of reactions 1 and 2 because of the known chemical similarity between SCN<sup>-</sup> and halide ion and the fact that HOX is the first product in peroxide/halide reactions.<sup>18</sup> HOSCN has also been postulated as an intermediate in the hydrolysis of thiocyanogen.<sup>19</sup> Nothing is known of the specific rates of reactions 3 and 5, but they are apparently fast enough relative to reaction 1 to be non-rate-determining. Reactions 7 and 8 are very rapid under the conditions of our studies,<sup>20,21</sup> and reaction 8 provides a sensible explanation of the oxygen-18 tracer experiment.

The acid-catalyzed process is accounted for by reactions 2, 3, 4, 6 and 8. The species HSCN and H<sub>3</sub>O<sub>2</sub><sup>+</sup> are not invoked in reaction 2 since the former is a very strong acid<sup>22</sup> and the latter is claimed to exist in only negligible concentration in dilute hy-

(17) O. Masson, *J. Chem. Soc.*, **91**, 1449 (1907).

(18) D. H. Fortnum, C. J. Battaglia, S. R. Cohen and J. O. Edwards, *THIS JOURNAL*, **82**, 778 (1960).

(19) W. Lecher, M. Wittwer and W. Speer, *Ber.*, **56B**, 1104 (1923).

(20) M. B. Jensen, *Acta Chem. Scand.*, **12**, 1657 (1958).

(21) P. M. Mader, *THIS JOURNAL*, **80**, 2634 (1958).

(22) M. Gorman and J. Connell, *ibid.*, **69**, 2063 (1947).

drogen peroxide solutions.<sup>23</sup> The kinetics of the reaction are accounted for by assuming reactions (6) and (8) to be much more rapid than (2), (3) and (4) and applying the "steady-state" hypothesis as regards HO<sub>2</sub>SCN to the latter three reactions. The resulting rate law is

$$R = \frac{1}{3} \left( \frac{dx}{dt} \right) = k_2(\text{H}_3\text{O}^+)(\text{SCN}^-)(\text{H}_2\text{O}_2)^2 / [(\text{H}_2\text{O}_2) + k_4/k_3(\text{HCN})] \quad (g)$$

where  $x$  is the total  $[(\text{H}_2\text{O}_2) + (\text{S}(\text{CN})_2)]$  as is determined by the iodometric technique (method A). It is seen that this expression corresponds exactly with (f) which was deduced above from iodometric rate data, provided  $\alpha = k_4/k_3 = 2$  and is more or less temperature independent, an entirely reasonable expectation.

The similarity between  $\text{SCN}^-$  and halide ion has been mentioned in regard to reactions 1 and 2. It is of interest that studies of the peroxide/iodide reaction<sup>24,25</sup> over a wide pH range lead to the rate expressions

(23) A. G. Mitchell and W. F. K. Wynne-Jones, *Trans. Far. Soc.*, **52**, 824 (1956).

$$R = k_1(\text{I}^-)(\text{H}_2\text{O}_2) \quad (\text{high pH})$$

$$R = k_2(\text{H}_3\text{O}^+)(\text{I}^-)(\text{H}_2\text{O}_2) \quad (\text{low pH})$$

These are identical in form with the expressions deduced in our studies for initial rates of the peroxide/thiocyanate reaction *in absence of HCN*. Furthermore, above an ionic strength of about 0.1, neither  $k_1$  or  $k_2$  of the iodide processes vary appreciably<sup>24</sup> with  $\mu$ , again corresponding with our findings. However, the analogy is seen to break down completely in the acid-catalyzed thiocyanate reaction as soon as (HCN) becomes appreciable. The expected product on the basis of the halide comparison is  $(\text{SCN})_2$ , a species for the presence of which no evidence whatsoever could be adduced in our work.

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(24) H. A. Liebafsky and A. Mohammad, *THIS JOURNAL*, **55**, 3977 (1933); *J. Phys. Chem.*, **38**, 857 (1934).

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## The Activation of Molecular Hydrogen by Platinum<sup>1</sup>

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The activation of molecular hydrogen by platinum has been studied by means of the *ortho-para* hydrogen conversion and the exchange reaction between hydrogen and deuterium oxide. The reaction between hydrogen and water has been shown to be a gas phase reaction. With 100% D<sub>2</sub>O as solvent, there was no *para* hydrogen conversion and D<sub>2</sub> was produced in greater quantities than HD. The data indicate that platinum catalyzes a homolytic split of the hydrogen molecule. The mechanism of the platinum catalyzed activation of hydrogen is compared with the enzyme catalyzed reaction.

In 1933, Horiuti and Polanyi<sup>2</sup> observed that platinum black catalyzed an exchange reaction between water and deuterium gas. They concluded that the deuterium gas is converted to ions by the catalyst which exchange with the protons of the water. Eley and Polanyi<sup>3</sup> compared the platinum black catalyzed *ortho-para* hydrogen conversion and exchange reaction between deuterium and water and found that the rate of the conversion reaction was two to three times that of the exchange reaction. They suggested that the rate determining process in both reactions was the splitting of the hydrogen molecule to ions or atoms in a strongly polar state. There was no evidence for a preliminary equilibrium between the hydrogen molecule and hydrogen atoms and the differences in the rates of the two reactions were attributed to the differences in the energies of hydrogen compared to deuterium. When the platinum black catalyzed exchange reaction and *para* hydrogen conversion

between 80% D<sub>2</sub>O and *para* hydrogen was studied by Farkas,<sup>4</sup> the conversion was found to proceed more slowly than the exchange. It was suggested that the dissociation of hydrogen was the rate limiting step and that ions, not atoms, are produced which exchange with the deuterium ions of the water more rapidly than the discharge of two ions and the subsequent recombination to normal molecules.<sup>5</sup>

During the course of the investigation of the mechanism of action of the enzyme hydrogenase, certain of the reactions catalyzed by the enzyme were also studied when catalyzed by platinum. This paper describes these findings, and although many of the reactions catalyzed by the enzyme and platinum are quite similar, the mechanism of hydrogen activation is different in these two systems.

### Experimental

The platinum oxide and platinum tetrachloride were purchased from Baker and Co., Newark, N. J. Deuterium gas and 99.9% D<sub>2</sub>O were purchased from the Stuart Oxygen Company on allocation from the Atomic Energy Commission.

(4) A. Farkas, *ibid.*, **32**, 922 (1936).

(5) The literature on the exchange reactions has been reviewed by T. I. Taylor in "Catalysis," Vol. V, P. H. Emmett, Editor, Reinhold Publishing Co., New York, N. Y., 1957, p. 257.

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