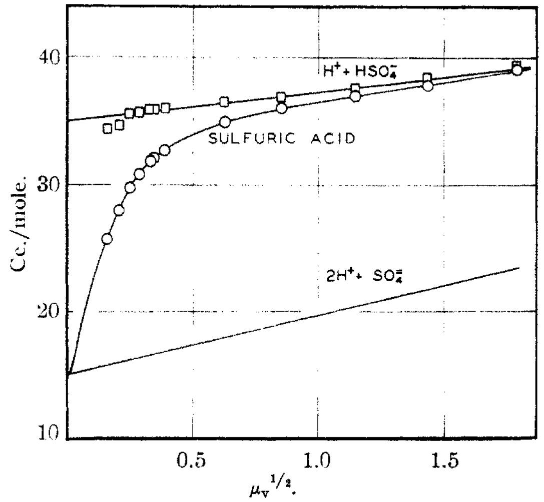

Fig. 1.—Apparent molal volumes of sulfuric acid and its constituents: O, observed volumes; □; calculated volumes.

Figure 1 shows the results for the calculated volumes of the constituents of sulfuric acid solutions as well as the experimental data. The curve for sulfuric acid in the very dilute range (up to $\mu^{1/2} = 0.15$) was calculated from the volumes of the ionic components and shows a definite cusp just beyond $\mu^{1/2} = 0$. The observed apparent molal volume rises very rapidly as the concentration is further increased because more and more bisulfate ion is formed. As we reach concentrated solutions ($\mu^{1/2} > 0.5$) the proportion of sulfate ions becomes progressively smaller and the observed volumes become, very nearly, those calculated for $(H^+)(HSO_4^-)$. Thus the observed volumes of sulfuric acid from 0 to 3 molar can be interpreted quantitatively in terms of the respective contributions of the constituent ions.

The Volume Change on Ionization of Bisulfate Ion.—Extrapolation to infinite dilution yields a value of 35.1 cc./mole for $\bar{V}^0$ of $(H^+)(HSO_4^-)$. Combining this figure with that for $(H^+)_2(SO_4^=)$ we find the volume change upon ionization of bisulfate ion at infinite dilution to be −20.2 cc./mole:

$$HSO_4^- = H^+ + SO_4^= \qquad \Delta \bar{V}_2^0 = -20.2 \text{ cc./mole}$$

Acknowledgment.—We are indebted to Professor Frank T. Gucker, Jr., and to Professor T. F. Young of the University of Chicago for a number of suggestions concerning the presentation of this material.

Summary

The densities of solutions of sulfuric acid have been determined over the concentration range of 0 to 3 molar and the apparent molal volumes interpreted in terms of the volumes of the hydrogen, sulfate and bisulfate ions.

The apparent molal volumes of hydrogen and bisulfate ions have been calculated by a series of successive approximations.

Evanston, Illinois Received April 21, 1942

[Contribution from the Frick Chemical Laboratory, Princeton University]

The Kinetics of the Thermal Reaction between Hydrogen and Cyanogen

By N. C. Robertson and R. N. Pease

Since the reactions of hydrogen with the various halogens have had such an important role in the development of chemical kinetics, it was thought that an investigation of the reaction with cyanogen might be profitable. The only reference to such a reaction is a report by Berthelot[1] that heating hydrogen and cyanogen in glass vessels in the neighborhood of 550° results in the formation of hydrogen cyanide together with a considerable amount of a polymer assumed to be paracyanogen.

The object of the present research was to establish the mechanism of this reaction in its relation to the other familiar reactions of hydrogen.

Experimental Procedure

The reaction was studied in a static system employing a silica vessel for most of the runs. This bulb, which was spherical and of some 550-cc. capacity, was placed at the center of a large electrically heated furnace which was provided with an auxiliary winding for the reaction chamber by means of which the temperature of the chamber was controlled to ±0.1° by a photoelectric potentiometer device connected to control thermocouples. The temperature was measured by means of two thermocouples immediately adjacent to the reaction vessel, heat losses and temperature gradient being minimized by packing the space for 10 inches above and below the reaction chamber with asbestos fiber. Apiezon was found to be satisfactory for stopcock lubrication.

Tank hydrogen was purified by passage over platinized

---

(1) M. Berthelot, *Compt. rend.*, **89**, 63 (1878).

asbestos at 350° and dried by condensing the water vapor in a trap surrounded by liquid air. Cyanogen was prepared by slowly dropping a concentrated solution of C. P. sodium cyanide onto powdered copper sulfate in a 500-cc. flask which was provided with a ground glass joint for the dropping funnel. The cyanogen was dried by passage through calcium chloride and was repeatedly fractionated from dry-ice and ether in an all glass system. Finally after admission to the storage vessel attached to the main vacuum system it was condensed several times in liquid air and the non-condensable gases evacuated with a mercury vapor pump. Cyanogen prepared by this method was found to contain only traces of hydrogen cyanide as shown by analysis, and the vapor pressure over dry-ice was that observed by Perry and Bardwell;[2] moreover, the consistency of the results obtained with a number of different preparations was considered good evidence for a reasonable degree of purity.

The hydrogen cyanide used in the experiments on inhibition was kindly furnished by Dr. J. Holmes of this Laboratory and was prepared by the action of sulfuric acid on sodium cyanide with subsequent drying and fractionation.

In making a run hydrogen as the lighter gas was first admitted to the thoroughly evacuated reaction chamber up to the desired pressure as indicated by a mercury manometer; then cyanogen was rapidly admitted from the storage bulb to give the desired total pressure. At the end of the run a sample amounting to approximately 60% of the reaction mixture was admitted to a previously evacuated analysis bulb of known volume, which was attached to the apparatus by a ground glass joint, the exact amount of the sample being determined by the pressure difference.

Since it soon became apparent that, aside from a small quantity of polymer, hydrogen cyanide was the only product formed in any substantial amount, the analytical procedure was designed to determine hydrogen and hydrogen cyanide. In order to determine hydrogen the cyanogen and hydrogen cyanide were condensed by surrounding the analysis bulb with liquid air and the hydrogen rapidly pumped off. The difference in pressure when the contents of the bulb had been allowed to return to room temperature was a measure of the hydrogen present since several experiments showed that no appreciable quantity of hydrogen dissolves in the condensed phase.

The determination of hydrogen cyanide in the presence of cyanogen was based on the method of Rhodes[3] and involves the rapid and quantitative reaction of hydrogen cyanide with a slightly acidified solution of silver nitrate with no interference by cyanogen. The analysis bulb was removed from the apparatus and inverted in a beaker containing a measured quantity of 0.025 *N* solution of silver nitrate to which one drop of dilute nitric acid per 5 cc. of solution had been added. By momentarily opening a stopcock a portion of this solution was allowed to flow up into the analysis bulb containing the cyanogen and hydrogen cyanide. The bulb was then shaken vigorously, opened, and the contents, consisting of precipitated silver cyanide and unreacted solution, washed out into the beaker with distilled water. The solution was then filtered and the remaining silver nitrate determined by titration with standard potassium thiocyanate using an indicator solution of ferric ammonium sulfate. From the silver nitrate neutralized by the hydrogen cyanide it was possible to calculate the pressure of hydrogen cyanide in the reaction vessel. Analysis of known mixtures and the consistent checks with the analysis for hydrogen showed this method to be accurate to 1%.

Results

The reaction was studied over the temperature range 550–675°; however, it proceeds at a very convenient rate at 625°, and the kinetic results were obtained at this temperature.

In order to show experimentally that equilibrium in the system

$$H_2 + (CN)_2 \rightleftarrows 2HCN$$

is far to the right, 0.5 atmosphere of hydrogen cyanide was allowed to stand for forty-eight hours at 625°. No decomposition could be detected on analysis although polymerization amounted to about 3%. It was concluded that the reaction as written is at least 98% complete.

About thirty runs were made in the silica vessel at temperatures of 500–600° before any attempt at accurate kinetic measurements. In view of the tendency of both cyanogen and hydrogen cyanide to polymerize in this region, it is probable that some polymer accumulated on the surface of the bulb. In a single run at any temperature above 600°, however, the pressure decrease was only of the order of magnitude of 0.5%. About sixty runs were made in this "aged" bulb, each series being bracketed by standard runs of 215 mm. of each reactant for a sixty-minute period at 625°. Typical kinetic results at this temperature are summarized in Table I-A.

The most prominent feature of the reaction is the emphasis upon the concentration of hydrogen. Constants for a three halves order and for a "Bodenstein–Lind" expression were calculated and are given in the table. The temperature coefficient in this bulb was determined over the range 575–675° (Table I-C) and corresponded to an over-all activation energy of 72 kcal. (Fig. 1).

Although the reaction appeared to be of low order as far as total pressure is concerned, the rate decreased rather rapidly with time, which suggested an inhibiting action by the product, hydrogen cyanide. To test this, pure hydrogen cyanide was added at the beginning of several runs with results recorded in Table I-B. Not

---

[2] J. H. Perry and D. C. Bardwell, THIS JOURNAL, **47**, 2629 (1925).

[3] F. H. Rhodes, *J. Ind. Eng. Chem.*, **4**, 652 (1912).

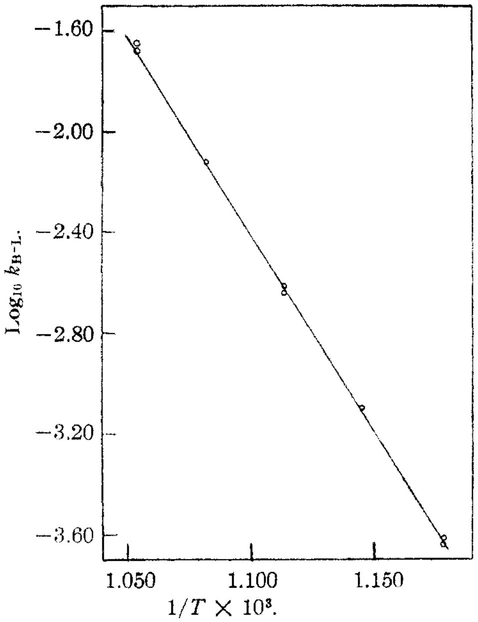

Fig. 1.—Activation energy in aged bulb.

only was the inhibiting action confirmed, but it was shown to be significantly greater when the ratio of the initial concentration of hydrogen to that of cyanogen was high.

Table I

Kinetic Results in Aged Bulb

A. Time and pressure dependence

Run no.	Time, min.	Mm. H_2 in	Mm. $(CN)_2$ in	Mm. HCN out	$k_{3/2}$ $\times 10^4$	$k_{B\text{-}L}$ $\times 10^{3a}$
		Approximately 100 mm. H_2–100 mm. $(CN)_2$				
93	30	103	105	39	6.94	3.00
72	60	100	105	67	7.33	3.17
77	120	100	100	96	6.46	2.82
		Approximately 205 mm. H_2–225 mm. $(CN)_2$				
40	2	204	249	(24)	(19.0)	(7.7)
37	15	195	224	63	(8.05)	(3.29)
38	30	208	230	102	6.39	2.70
79	60	206	225	150	5.50	2.29
66	120	207	226	223	5.00	2.25
41	240	207	238	293	4.27	2.27
		Approximately 305 mm. H_2–325 mm. $(CN)_2$				
55	30	304	319	162	6.19	2.29
56	60	302	335	249	5.84	2.33
57	120	305	337	360	5.03	2.33
		Approximately 310 mm. H_2–110 mm. $(CN)_2$				
51	2	312	106	(16)	(12.8)	(5.18)
91	30	305	111	74	4.51	1.91
90	60	307	110	132	4.98	2.27
76	120	320	112	180	3.68	1.98
75	180	319	105	188	2.95	2.10
		Approximately 105 mm. H_2–320 mm. $(CN)_2$				
50	2	101	311	(22)	(32.8)	(13.2)
92	30	104	325	59	6.45	2.60
89	60	107	319	84	4.88	2.10
43	120	103	329	136	5.30	2.21
74	180	106	320	160	4.64	1.80

[a] *k*'s are for the units millimeters and minutes.

B. Inhibition by hydrogen cyanide. All runs for 60 minutes at 625°

Run no.	Mm. H_2 in	Mm. $(CN)_2$ in	Mm. HCN in	Mm. HCN produced
86	223	221	0	158
85	220	225	100	143
87	218	227	196	134
90	307	110	0	132
81	309	111	98	113
89	107	319	0	84
80	105	311	98	81
72	100	105	0	67
94	103	101	203	57

C. Temperature dependence

Run no.	Temp., °C.	Time, min.	Mm. H_2 in	Mm. $(CN)_2$ in	Mm. HCN out	$k_{B\text{-}L}$ $\times 10^{3a}$
62	575	720	205	228	168	0.230
64	575	921	204	222	189	0.225
61	600	360	205	242	236	0.797
65	625	60	207	230	157	2.41
66	625	120	207	226	223	2.25
59	650	35	206	234	226	7.51
58	675	10	203	230	209	23.5
63	675	10	207	241	202	21.2

D. Precision of measurements. Bracket runs at 625° for 60 min.

Run no.	Mm. H_2 in	Mm. $(CN)_2$ in	Mm. HCN out	$k_{B\text{-}L}$ $\times 10^{3a}$
36	206	226	148	2.25
42	217	210	156	2.41
49	208	225	150	2.34
60	208	217	154	2.46
65	207	230	157	2.41
70	207	238	152	2.22
79	206	225	150	2.29
88	206	231	154	2.34
95	204	223	148	2.29

[a] *k*'s are expressed in the units millimeters and minutes.

In several experiments 1–2 mm. of oxygen was added to the reaction mixture, in which instance the rate was observed to increase by about 75%; however, no evidence for catalysis by minute traces of oxygen, such as characterizes the vapor phase reactions of many organic substances, was obtained.

An early observation that the rate in Pyrex at 550° is some 50% higher than in clean silica indicated a qualitative effect of surface. In order to study the quantitative influence, the reaction vessel was removed, treated with concentrated nitric acid to cleanse the surface of any film of polymer, washed with distilled water and packed with clear silica tubing of 10-mm. diameter which had been cleaned by prolonged treatment with hot nitric acid. This packing increased the surface–volume ratio by a factor of 3.5–4, and its surface was considered to be the best obtainable duplication of that of the blown silica vessel. Since it developed that cleaning the surface causes some alteration in the rate and temperature coefficient of the process, a series of runs was made in the acid-cleaned unpacked bulb for purposes of comparison.

Although preliminary results in the packed bulb were erratic and somewhat high, the rates quickly settled down and became reproducible. A puzzling complication was encountered in that after raising the temperature from 550 to 625° or higher, it was necessary to make several runs followed by periods of extended pumping before the rate at the higher temperatures rose to a consistent value. On account of the greater pressure decrease during low temperature runs, it may be possible to attribute this to the formation of paracyanogen on the walls since this is said to occur in the range 500–600°. The consistent rates are given in Table II-A for standard runs at several temperatures in comparison with runs in the empty vessel after the packing had been removed. It is apparent that packing increases the rate at low temperatures somewhat, while causing no appreciable change at 650 or 675°. This makes it highly improbable that the reaction is entirely a surface process; however, it would seem to indicate either that at the lower temperatures there is a concurrent reaction proceeding on the surface or that the wall participates in some step of a gas phase process.

Since the nature of the surface is obviously of considerable importance to the kinetics, a means of treating it so that its function could be studied to better advantage was sought. It had been observed that treating the aged bulb with oxygen caused no substantial change in the rate; however, when the packed bulb was treated at 675° for two hours with an atmosphere of pure oxygen and then thoroughly evacuated, the rate was very decisively decreased at all temperatures, as may be seen from Table II-B. When the packing was removed, this procedure had no effect on the rates in the empty bulb. This seeming anomaly may be due to a qualitative difference between the surface of the packing and that of the bulb itself, but the fact that the rate in the packed bulb after oxygen treatment is less than in the unpacked bulb is considered most significant. It is plausible that oxygen at such high temperatures would strip any adsorbed film from the surface although this may not be its sole action.

TABLE II

EFFECT OF SURFACE

A. Comparison of rates in packed and unpacked bulbs. All runs with approximately 205 mm. H_2–225 mm. $(CN)_2$

		Packed Bulb (b)			Unpacked Bulb (b)		
Temp. °C.	Time, min.	Mm. H_2 in	Mm. $(CN)_2$ in	Mm. HCN out	Mm. H_2 in	Mm. $(CN)_2$ in	Mm. HCN out
550	1140	206	230	234	206	228	178
625	60	208	227	238	209	231	216
	60	206	228	241	206	245	214
650	20	206	230	191	208	230	183
675	10	207	235	170	206	232	180
					207	235	187

B.

		Oxygen treated packed bulb			Oxygen treated unpacked bulb		
550	1140	205	232	53	206	228	178
625	60	207	235	78	210	233	210
650	20	206	242	40	207	240	172
	20	206	235	28			

C. Pressure dependence in unpacked bulb[b]

Run no.	Temp., °C.	Time, min.	Mm. H_2 in	Mm. $(CN)_2$ in	Mm. HCN out	$k_{B\text{-}L} \times 10^3$	$k' \times 10^2$[a]
137	625	60	103	107	103	6.18	1.251
148	625	60	209	231	216	3.89	1.217
149	625	60	310	313	300	3.31	1.222
135	625	60	312	108	187	4.89	0.811
136	625	60	103	320	109	3.03	1.290
145	675	10	102	108	82	18.5	...
144	675	10	206	235	187	15.3	...
146	675	10	316	328	305	14.3	...

[a] k's are expressed in the units millimeters and minutes.

[b] After nitric acid treatment.

A few runs with varying initial pressures of reactants were made in the unpacked bulb following oxygen treatment. The kinetics at 625° (Table II-C), although not markedly different from those in the aged bulb seem to require a somewhat lower power of the cyanogen concentration (see Discussion). The fact that the temperature coefficient is lower than in the aged bulb may be taken to indicate increased participation by the surface in some phase of the reaction.

Discussion of Results

With regard to the reaction kinetics, the following facts are outstanding: the existence of a brief period of rapid reaction when the gases are first introduced, the greater dependence upon the hydrogen concentration during the further course of the reaction, the inhibiting effect of the product, and the low order of the reaction with respect to total pressure.

A second-order expression of the hydrogen–iodine type was implausible on account of the low order of the reaction and the necessary dominance of the hydrogen concentration in any kinetic expression.

Constants for a three halves order equation involving the square root of the cyanogen concentration (Table I-A, Column 6) fall sharply with time when the ratio of hydrogen to cyanogen is high. This, together with the inhibition by hydrogen cyanide, pointed to the well-known Bodenstein–Lind[4] type of expression developed for the reaction of hydrogen and bromine

$$\frac{d[\mathrm{HCN}]/2}{dt} = \frac{k_{\mathrm{B\text{-}L}}\,[\mathrm{H_2}][(\mathrm{CN})_2]^{1/2}}{1 + m\,\dfrac{([\mathrm{HCN}]/2)}{[(\mathrm{CN})_2]}}$$

The constants, calculated for $m = 0.25$ and expressed in millimeters and minutes, are listed in column 7 of Table I-A, the values of the constants for some fifty runs falling within the range shown. This expression is the simplest one which fits the kinetics in the aged bulb reasonably well. Aside from its neglect of the period of initial acceleration, it is deficient only in the high values of the constants for runs with low total pressures. Quite possibly this may be attributed to a surface reaction of very low order; for, if 5–10 mm. of product per hour were formed by a zero-order reaction, the constants for runs with 100 mm. of each reactant would become compatible with those for higher pressures. For runs at low pressures or for high ratios of one reactant to the other the integrated expression is extremely sensitive, and this accounts for most of the observed fluctuations.

Since the packing experiments showed that the reaction is not heterogeneous, the applicability of the Bodenstein–Lind equation, the inhibition by product, and the strong inhibition by the packing in the oxygen-treated bulb are cogent arguments for a reaction involving chains propagated by free radicals and atoms. The acceleration by a small concentration of oxygen is also a type of phenomenon frequently encountered when chain processes are involved.

The most elementary mechanism, by analogy with the hydrogen–bromine reaction, is

$$(\mathrm{CN})_2 \longrightarrow 2\mathrm{CN} \qquad (1)$$
$$\mathrm{CN} + \mathrm{H_2} \longrightarrow \mathrm{HCN} + \mathrm{H} \qquad (2)$$
$$\mathrm{H} + (\mathrm{CN})_2 \longrightarrow \mathrm{HCN} + \mathrm{CN} \qquad (3)$$
$$\mathrm{H} + \mathrm{HCN} \longrightarrow \mathrm{H_2} + \mathrm{CN} \qquad (4)$$
$$\mathrm{CN} + \mathrm{CN} \longrightarrow (\mathrm{CN})_2 \qquad (5)$$

which leads by the familiar steady state solution to the equation

$$\frac{d[\mathrm{HCN}]/2}{dt} = \frac{2k_2\sqrt{k_1/k_5}\,[\mathrm{H_2}][(\mathrm{CN})_2{}^{1/2}}{1 + \dfrac{k_4}{k_3}\,\dfrac{[\mathrm{HCN}]}{[(\mathrm{CN})_2]}}$$

The propagation of the chains almost certainly centers around reactions 2, 3 and 4, and the necessity for introducing the one-half power of the cyanogen concentration is good evidence for chain ending by a recombination of two CN radicals. The feasibility of chain initiation by the dissociation of cyanogen molecules into free radicals as in equation 1, however, must be determined by other considerations; for, if this is the case, the maximum concentration of cyanide radicals is that attained when the reversible dissociation of cyanogen has reached equilibrium. In order to determine whether this equilibrium concentration is sufficient to give the observed absolute rate of reaction the simple collision theory treatment used by Morris and Pease[5] in considering the thermal hydrogen–chlorine reaction may be employed. The rate of formation of hydrogen cyanide, neglecting the inhibiting action by the product through reaction 4, is calculated as

$$\mathrm{d}n_{\mathrm{HCN}}/\mathrm{d}t = 2k_2\sqrt{K_{\mathrm{eq.}}}\,\sqrt{n_{(\mathrm{CN})_2}}\,n_{\mathrm{H_2}}$$

where the n's are the numbers of hydrogen and cyanogen molecules, k_2 is the rate of the reaction

$$\mathrm{CN} + \mathrm{H_2} \longrightarrow \mathrm{HCN} + \mathrm{H} \qquad (2)$$

and $K_{\mathrm{eq.}}$ is the equilibrium constant for the dissociation

$$(\mathrm{CN})_2 \rightleftarrows 2\mathrm{CN}$$

According to collision theory k_2 is given by

$$k_2 = 2\left[2\pi R\,\frac{M_1 + M_2}{M_1M_2}\right]^{1/2} \sigma_{12}{}^2\, T^{1/2}\, e^{-E/RT}$$

A value of 7 kcal. for E, the activation energy of reaction 2, has been reported by Hartel and Polanyi[6] from their studies of highly dilute flames. The radius of hydrogen is taken from viscosity data as 1.09 Å. and that of the CN radical as 1.50 Å. or slightly less than that of the nitrogen molecule[7] which should occasion no serious error. Substitution of these values gives $k_2 = 1.34 \times 10^{-11}$ in cc. per molecule per second at 900°K.

Unfortunately, reports of the heat of dissociation of cyanogen into radicals are contradictory. The value 77 kcal. was determined by Kistiakowsky and Gershinowitz.[8] More recently White[9] has assigned 137 kcal. as a minimum value with a probable value of 146 kcal. White has also calculated the entropy change in the dissociation as a function of temperature making use of the best available spectroscopic data; and from this the free energy change and equilibrium constant at

---

[4] (a) M. Bodenstein and S. C. Lind, *Z. physik. Chem.*, **57**, 168 (1907); (b) C. N. Hinshelwood, "Kinetics of Chemical Change," Oxford Press, New York, N. Y., 1940, p. 102.

[5] J. C. Morris and R. N. Pease, This Journal, **61**, 391, 396 (1939).

[6] H. v. Hartel and M. Polanyi, *Z. physik. Chem.*, **B11**, 97 (1930).

[7] Landolt-Börnstein, "Tabellen," E-g. I, 1927, p. 69.

[8] G. B. Kistiakowsky and H. Gershinowitz, *J. Chem. Phys.*, **1**, 432 (1933).

[9] J. U. White, *ibid.*, **8**, 79, 459 (1940).

any temperature not far from 1200°K. may be evaluated if the heat of dissociation is known.

Using the value 77 kcal., which is almost certainly too low, and calculating the equilibrium constant by means of White's equation, dn_{HCN}/dt is 5.4×10^6 mm./min. for a reaction mixture of 215 mm. each of hydrogen and cyanogen at 900° K. With White's value of 137 kcal. the rate is calculated as 0.30 mm./min. These calculated rates, whose validity depends upon the 7 kcal. activation energy for reaction 2, bracket the observed "steady" rate, the rate after the period of initial acceleration, of 2 mm./min.

It is possible that White's value may be somewhat high. Hogness and T'sai[10] concluded from their studies on the photochemical polymerization of cyanogen that 2240 Å., corresponding to 127 kcal., is the longest wave length of a cyanogen absorption band and is sufficient to give dissociation into CN radicals. If this value is taken, the equilibrium rate of formation of hydrogen cyanide, assuming again that reaction 2 requires 7 kcal. activation energy, becomes 4.5 mm./min. in better agreement with experiment.

It is also noteworthy that on the assumption of chain starting by dissociation of cyanogen it should be possible to obtain the over-all activation energy as the sum of half the heat of dissociation plus the activation energy of step 2. With the values 127 kcal. and 7 kcal., respectively, the over-all activation energy should be 71 kcal., in good agreement with the observed value of 72 kcal. From another standpoint, however, this is most significant in that it shows the experimental activation energy to be consistent with the proposed mechanism. Thus if the activation energy for step 2 as observed by Hartel and Polanyi is too high by several kilocalories, a larger heat of dissociation could be admitted; if it is too low, a value of even less than 127 kcal. would be necessary to account for the observed over-all activation energy and rate.

If the heat of dissociation of cyanogen is very large, the question of why the reaction does not proceed by the initial dissociation of hydrogen, which requires only 103 kcal., arises. Using White's equation for the entropy change, the equilibrium concentration of CN radicals would be equal to that of hydrogen atoms only if the heat of dissociation of cyanogen were as low as 114 kcal. If the starting involved the dissociation of hydrogen, however, the rate of reaction 3 would determine the absolute rate of formation of hydrogen cyanide; and this, for an equilibrium concentration of hydrogen atoms, may be so low compared to that of reaction 2, for an equilibrium concentration of CN radicals, that the hydrogen dissociation would be of minor importance in the conversion. This would imply that the activation energy of reaction 3 is larger than that of reaction 2, which is reasonable when the large energy of the carbon–carbon bond in cyanogen is considered.

It must be emphasized that these considerations show only that chain initiation by the direct dissociation of cyanogen into cyanide radicals is well within the realm of possibility. The final decision must wait upon the clarification of the uncertainties already mentioned when new data become available.

If chains are initiated by the dissociation of cyanogen molecules, then they must certainly start on the walls of the vessel since an elementary collision theory calculation shows that the time required to attain an equilibrium concentration of CN radicals by gas phase dissociation is of the order of magnitude of several days; furthermore if the walls act as a catalyst for the dissociation, they must also catalyze the chain ending process of recombination.

In view of the complexity of the reaction, however, chain initiation by some process other than the direct dissociation of cyanogen, by means of which a concentration of radicals greater than the equilibrium concentration could be furnished, must not be ruled out. Such a process might be a reaction between cyanogen and adsorbed hydrogen similiar to a mechanism suggested by Morris and Pease for chain starting in the hydrogen–chlorine reaction in one of their Pyrex bulbs.

$$\mathrm{WH_2} + \mathrm{(CN)_2} \longrightarrow \mathrm{WHCN} + \mathrm{H} + \mathrm{CN}$$

For strong adsorption of hydrogen this leads to a Bodenstein–Lind type of expression.

Too few runs in which there were wide variations in the initial pressures were made in the oxygen treated empty bulb to warrant broad generalizations with regard to the kinetics. The expression

$$\frac{d[\mathrm{HCN}]/2}{dt} = \frac{k'[\mathrm{H_2}]}{1 + m\,\dfrac{([\mathrm{HCN}]/2)}{[(\mathrm{CN})_2]}}$$

seems to fit the data at 625°, the constants for $m = 0.25$ and again expressed in terms of milli-

---

[10] T. R. Hogness and Liu-Sheng T'sai, THIS JOURNAL, 54, 123 (1932).

meters and minutes appearing in column 7 of Table II-C. The low value for the one run with a 3–1 initial ratio of hydrogen to cyanogen is understandable since by the end of the run practically all the cyanogen has reacted. Bodenstein–Lind constants, however, fit the variation with respect to total pressure at 675°, and the fit would be better if a lower value of *m* were taken for this temperature; but they are totally unsatisfactory at 625°.

Since there is no reason to suppose that the steps in chain propagation are any different in the clean bulb, the increased rate at low temperatures along with the lower temperature coefficient argues for a different method of chain starting on the surface. The possibility

$$WH_2 + W(CN)_2 \longrightarrow WHCN + H + CN$$

which results in the foregoing kinetic expression suggests itself since Hadow and Hinshelwood[11] obtained evidence of strong adsorption of cyanogen on clean silica in their oxidation studies.

Hogness and T'sai[10] found that CN radicals disappear at room temperature by addition to cyanogen molecules to form a postulated $(CN)_3$ which acts as a nucleus for further polymerization with the ultimate formation of paracyanogen. White[9] concluded that the radicals formed during an electric discharge combine with complex ions simultaneously produced in the discharge as a first step in polymerization. In the present investigation at temperatures of 625° or higher such an addition reaction was not indicated by kinetic analysis of the results in the aged bulb, nor was any extensive polymerization observed. This must mean that the reactions

$$CN + H_2 \longrightarrow HCN + H$$

and

$$CN + CN + W \longrightarrow (CN)_2 + W$$

are much faster than the addition of radical to molecule. It may well be that the $(CN)_3$ complex is unstable at these temperatures since it is known that cyanogen does not polymerize at elevated temperatures and that paracyanogen begins to regenerate cyanogen in the region 700–800°.

Summary

The thermal reaction of hydrogen and cyanogen to yield hydrogen cyanide has been studied in a silica vessel over the temperature range 550–675°. The reaction proceeds without undue complications, but the nature of the surface of the reaction bulb has some influence on the rate. The product, hydrogen cyanide, inhibits the reaction. Packing increases the rate at low temperatures but has little effect above 625°.

The simplest expression which fits the kinetics at 625° reasonably well is that developed by Bodenstein and Lind for the combination of hydrogen and bromine. Evidence is presented which favors a radical chain mechanism involving gas phase propagation by hydrogen atoms and cyanide radicals with chains starting and breaking on the walls. The steps in this process would be analogous to those in the hydrogen–bromine reaction with the cyanogen assuming the role of bromine.

Princeton, New Jersey Received May 6, 1942

---

[11] H. J. Hadow and C. N. Hinshelwood, *Proc. Roy. Soc.* (London), **A132**, 375 (1931).

[Contribution from the Avery Laboratory of Chemistry of the University of Nebraska]

The Ternary Systems Involving Cyclohexane, Water, and Isopropyl and Normal Propyl Alcohols

By E. Roger Washburn, Charles E. Brockway, C. Loren Graham and Philip Deming

The ternary systems[1] made up of cyclohexane, water, and[1a] methyl and[1b] ethyl alcohols have been described previously.

The systems[2] involving water, isopropyl alcohol and[2a] benzene,[2b] toluene and[2c] cyclohexene have been described.

This report adds normal propyl and isopropyl alcohols to the first group and cyclohexane to the second group.

Materials.—Cyclohexane from Eastman Kodak Company was carefully fractionated, dried with sodium and recrystallized several times. The alcohols were the best grades obtainable from the same company. They were dried with active lime and carefully fractionated. Some physical

---

[1] E. R. Washburn, *et al.*, This Journal, (a) **56**, 361 (1934); (b) **54**, 4217 (1932).

[2] E. R. Washburn, *et al.*, *ibid.*, (a) **57**, 303 (1935); (b) **62**, 579 (1940); (c) **62**, 1454 (1940).