Summary

1. Ketene has been found to polymerize to diketene between 400 and 500°, the polymerization decreasing rapidly with increasing temperature. An attempt to find the equilibrium constants was unsuccessful.

2. Above 530° ketene has been found to decompose chiefly into carbon monoxide and methane, depositing a carbon-like mass, and yielding three molecules of gaseous reaction products for every two molecules of decomposed ketene.

3. For the first 10% of its course the decomposition is of 1.5th order, after which it loses speed and cannot be made to fit any simple kinetic expression.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Activation of Gases by Metals

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Some time ago the former of us discovered that if various metals, even when in a high state of purity, are heated in gases like hydrogen, nitrogen, helium, argon or carbon dioxide, a very disagreeable odor is produced which is not observed under otherwise like experimental conditions when the metal is absent. This odor, while not perfectly identical in all cases, is nevertheless always very similar in nature and is perhaps best described as a burnt odor of nitrogenous character.

The present investigation was undertaken to ascertain the causes of this odor and to determine why hydrogen, when passed over hot metals, apparently acquires the ability to unite with sulfur at ordinary temperatures and to reduce ferric salts, permanganate and blue starch iodide.

Very much exceedingly careful detailed work was done on this subject which occupied almost two years. For the sake of brevity, only the essentials of the experimental methods and the results obtained will be presented.

Experimental

The metals were heated in a combustion tube 100 cm. long and 2 cm. in internal diameter. The tube was of Scotch glass. It was thoroughly cleaned and dried and hydrogen at red heat passed through it until it was perfectly odorless, before any metal was inserted. The metals were commonly heated in the tube in a scrupulously clean porcelain combustion boat. The latter was, of course, first heated empty in the tube until all traces of odor were gone before any metal was introduced. The sulfur, permanganate, ferric chloride or blue starch iodide paper was commonly placed in another clean porcelain boat in the cooled end of the tube about 5 to 10 cm. from the boat containing the hot metal. The heating was accomplished in an ordinary combustion furnace. Tubes of Pyrex glass, Jena glass, German combustion tube glass and porcelain were also employed. The results were always the same. The heating was also tried by means of electric coils instead of the gas combustion furnace. Again the results were always the same. Furthermore, heating the metals by arcing them in the gas in question also produced the same identical effects. It was thus comparatively easy to get suitable containers and methods of heating. It was also relatively easy to obtain the gases of sufficient purity. They were carefully prepared by standard methods and then passed through a series of purifying solutions and drying towers before they entered the combustion tube.

The chief experimental difficulty was encountered in the metals themselves, that is to say, in getting them of sufficient purity. By taking the very best obtainable so-called C. P. metals of standard manufacturers, or by employing metals prepared carefully here in the laboratory, it was found that all of the following gave off hydrogen sulfide when heated in pure hydrogen gas: Al, Co, Cu, Au, Fe, Mg, Ni, Pt, Ag, Pd, Sn, Zn, Cd, W, Pb, In, Si, Cb, Cr, Ta, As, Sb, Bi. Moreover, they all produced the burnt odor mentioned. These odors lasted variously from ten minutes, in the case of Pd, to eight hours in the case of Ni. The odors also varied in intensity. As long as the odor lasted the gas exhibited reducing power on permanganate, ferric salts and blue starch iodide; it also always darkened lead acetate paper, showing the presence of hydrogen sulfide. The burnt odor commonly disappeared long before the lead acetate reaction for hydrogen sulfide ceased. The presence of the latter gas showed that small amounts of sulfur were contained in all of the metals tested.

So far as the burnt odor is concerned, it was observed not only when hydrogen was employed but also when nitrogen, helium, carbon dioxide or oxygen was used. With the latter gas the odor was faint and very soon disappeared entirely. When the odoriferous gas was passed over red-hot copper oxide and then conducted into lime or baryta water a turbidity was obtained, clearly demonstrating the presence of carbon.

It was found that metals heated in a current of gas until the latter was completely odorless and then cooled and kept in that same gas or in purified air, would not again produce the odor on heating them. Neither would they

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again yield hydrogen sulfide if they had been heated in hydrogen until the hydrogen sulfide reaction on lead acetate paper had ceased and then kept in pure hydrogen, or purified air, until heated again in hydrogen. However, when exposed to the air of the laboratory, or to outdoor air, even for a few minutes, they again acquired the power of producing both the odor and the hydrogen sulfide reaction. This is true even of such metals as platinum[3] and gold. It was therefore perfectly clear that the metals adsorb sulfur compounds from the air, and it was also indicated that they gather up particles of dust laden with microörganisms and that the latter on heating give rise to the burnt nitrogenous odors observed. This also at once explained why the odor was slight when the metals were heated in oxygen and very soon disappeared entirely, for the bodies of the microörganisms were completely and rapidly oxidized[4] to odorless products.

The question arose as to whether different metals have different specific attraction for microörganisms. To answer this, carefully cleaned and sterilized strips of foil of each of the following pure metals: Au, Al, Cu, Pt and Pd, were exposed to the air of the laboratory for twelve hours. After such exposure the organisms on each piece were cultured on veal infusion agar and incubated at 37° using regular bacteriological procedure at all times. The agar plates were examined for growth regularly for six days and the colonies counted. Two runs were made. The area of each piece of metal was about 25 sq. cm. and by way of control a clean, white, sterilized piece of porcelain of about equal area was run simultaneously as a control. No evidence was found that the metals have any specific attraction for or killing power for microörganisms, when tests were made as described. An abundance of microorganisms was, of course, found on the metals as well as on the porcelain control, as was to have been expected.[5] Yeast or molds were not found to be present, however. It should be remarked in this connection that porcelain, glass and tile which have been exposed to the air also yield a burnt odor when similarly heated in combustion tubes in the gases above mentioned, on account of the microorganisms they gather on their surfaces. Nevertheless, the odors produced by the metals always seemed more pronounced, possibly because the organic material they gathered was decomposed more readily and somewhat differently on their hot surfaces. It is, of course, also to be borne in mind that many of the so-called C. P. metals contain small amounts of carbon as well as tiny amounts of sulfur due to their origin and preparation; and these ingredients doubtless also affect the odor produced. This was noticed particularly with samples of aluminum, nickel and bismuth when heated in hydrogen.

It should be remarked that it was found that exposure of pure metals to an atmosphere of pure carbon dioxide does not lead to production of the odor on subsequent heatings in hydrogen, nitrogen, etc.; so that the odor is not to be laid to the carbon dioxide in the air, which is, of course, always present on the surfaces of metals.

In order to get at the bottom of the question in hand, it was deemed desirable to make a very elaborate, intensive study of the behavior of a very highly purified metal in pure hydrogen. Silver was chosen, for it is well known that it can be prepared easily in very pure form. This metal was prepared electrolytically from the pure nitrate, also by reduction of pure silver chloride and pure silver oxide, and again by ignition of pure silver tartrate in oxygen. All of these samples yielded identical results. The hydrogen was prepared electrolytically, and also by action of pure electrolytic zinc on pure dilute hydrochloric acid. The gas was passed through alkaline pyrogallol, concentrated sulfuric acid and towers of calcium chloride and fused caustic potash before it was conducted over the pure, hot metal in the combustion tube. Special care was taken to exclude the possibility of carrying any particles of the purifying train over into the combustion tube mechanically. Blanks on the tube, the porcelain boat and the hydrogen were always run before the pure metal was introduced.

In all cases the samples of silver when heated in pure hydrogen gave off hydrogen sulfide and the characteristic burnt odor. However, if after these phenomena had disappeared the metals were cooled in hydrogen and carefully kept in the latter, they never again on heating in hydrogen yielded hydrogen sulfide or the burnt odor. Neither was the resulting hydrogen active chemically toward sulfur, ferric salts, permanganate or blue starch iodide. Again, if the silver was heated in washed and purified air, or in pure oxygen, nitrogen or carbon dioxide and then kept in either of these gases, it never yielded either hydrogen sulfide, odor or "chemically active" hydrogen when subsequently heated in a current of pure hydrogen gas. However, the slightest, even momentary, exposure of the metal to the air of the laboratory, to outdoor air, or to air of a desiccator always resulted in a positive test for hydrogen sulfide and the odor. The slightest touch of the silver with the hands or even with a glass rod that had not previously been purified by heating to redness, sufficed to yield the hydrogen sulfide test with lead acetate paper upon subsequent heating of the silver in pure hydrogen. We were astounded by this ability of silver to adsorb notable amounts of sulfur compounds from the air or from articles that had been in contact with ordinary air. Bach[3] calls attention to a similar behavior of pure platinum with which he worked.

As already stated, the hydrogen was chemically active only as long as the odor persisted and the lead acetate test was positive. Hence this "activity" was due to impurities, as explained. It was deemed desirable nevertheless to test the hydrogen spectroscopically while the odor was strong and compare its spectrum with that of quite pure, odorless hydrogen. Vacuum tubes were constructed using pure silver electrodes so as to eliminate any effect that a foreign metal might have. The photographs of the visible portion of the spectra were taken on Eastman

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(3) Compare in this connection the splendid work of A. Bach, *Ber.*, **58**, 1388 (1925), on pure platinum. He makes similar observations as to the power of this metal to pick up sulfur compounds from the air. See also M. Scanavy-Grigoriewa, *Z. anorg. Chem.*, **159**, 55 (1927).

(4) Bach, Ref. 3, explained some of the results he obtained with platinum by assuming that the latter absorbed oxides of nitrogen from the air as well as sulfur compounds. It would seem that dust particles laden with bacteria, yeast and other microörganisms were perhaps the source of the nitrogen.

(5) For this careful biological work we are indebted to Professor W. D. Frost and his assistant, Miss Ruth Menges, of the department of bacteriology.

"Diaphax" x-ray films, while those in the ultraviolet were taken with Eastman special process films. In this latter case tubes of quartz, and a quartz spectrograph, of course, had to be employed, and it was also found necessary to make exposures for fifteen minutes because of the rather low intensity of the light source. Spectrum pictures were also taken with similar tubes in which the electrodes were of aluminum, gold and cadmium, respectively. The results in all cases were identical: namely, that no difference in the spectra of the "odoriferous" hydrogen and the pure hydrogen could be detected. A slight difference in intensity of some of the lines was occasionally apparent but that was all. Even when electrodes previously cathodically electrolytically laden with hydrogen in dilute phosphoric acid solution were employed in the vacuum tubes, the spectrum remained the same. In one single case in which pure nickel electrodes electrolytically laden with hydrogen were employed a line was found that was not in the spectrum of the pure hydrogen. The wave length of this line was approximately 2740; however, there is a well-defined phosphorus line at 2739, so that the observed line was doubtless due to phosphorus carried over from the electrolytic phosphoric acid bath. Hydrogen was thus thoroughly examined spectroscopically not only after it had been passed over silver, but samples that had coursed over hot Al, Au, Sn, Ni, Pd and Cr were also tested, with the same results. Introduction of a trace of benzene vapor into one of the tubes at once made a pronounced difference in the spectrum. The results of all of this painstaking spectroscopic work show that one cannot by this means find any difference between pure hydrogen and hydrogen that has passed over hot metals, the impurities picked up and present in the highly attenuated gas in the vacuum tubes being present in far too small an amount to exhibit their presence in the photographs of the spectra.

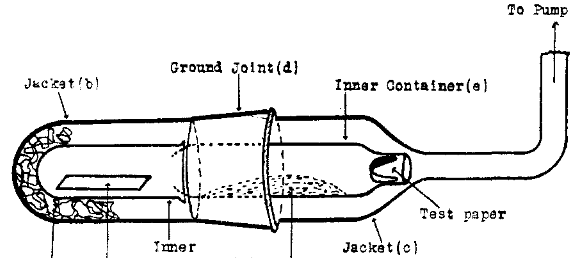

Fig. 1.

The fact that the so-called chemical activation of hydrogen by hot metals is really due to impurities in the latter or adsorbed on their surfaces from objects that have been in contact with them or from the air, is extremely important in evaluating the work of previous investigators who have often used large metallic cathodes, especially aluminum cathodes, in vacuum tubes. Under these conditions when the electrodes become heated, the impurities would doubtless be released and thus easily lead to erroneous experimental conclusions.

We wish to emphasize in this connection that the aluminum we used was of a very high grade of purity, namely, 99.7%. It was kindly furnished us by Dr. F. C. Frary of the Aluminum Company of America. This sample, however, yielded powerful odors and hydrogen sulfide tests. The carbon content of these odors could be detected by means of baryta water after the gas had been conducted over red-hot copper oxide. Yet this was from a sample of aluminum which was probably much purer than that at the disposal of earlier investigators.

By the experiments described above it has been demonstrated definitely that pure hydrogen at atmospheric pressure after passing over hot metals which are pure and absolutely free from all sulfur and organic contaminations shows no reducing action on roll sulfur, ferric chloride solution, potassium permanganate solution or blue starch iodide paper. On the other hand, by very careful experiments we found that hydrogen freshly liberated from certain cathodically hydrogenated elements was chemically active as manifested by its reducing action on dry, powdered roll sulfur (at temperatures ranging from 65 to 100°) placed at distances even as far as 15 cm. from the hydrogenated element.

The cathodically hydrogenated elements which yielded such active hydrogen are palladium, nickel, silicon, Acheson graphite and coconut charcoal. The experimental procedure was briefly as follows. The element selected, usually a strip 1.5 by 4 cm., was employed as cathode in dilute (1 to 20) phosphoric acid solution for thirty minutes at a current density of 10 amperes per sq. dcm., after which it was removed quickly from the bath, rinsed in distilled water, dried with filter paper and finally inserted in a scrupulously clean Pyrex glass container which in turn was placed in a definite position in another larger glass tube containing the dried roll sulfur and moist lead acetate paper. Figure 1 shows the essential features of the apparatus. Extreme care was used to prevent contamination of the hydrogenated element by sulfur compounds or organic impurities during the transfer or by the sulfur in the tube.

The entire, carefully assembled, gas-tight apparatus was then immersed in a water-bath at the desired temperature (65 to 100°) and the system evacuated to 3 to 5 mm. pressure. Thus the hydrogen was liberated from the cathodically hydrogenated element and passed over the roll sulfur and impinged on the test paper. The latter was examined at the end of ten minutes. Many careful blank runs were made so as to be sure that the actual observations were not due to impurities. For instance, ordinary hydrogen passed over the sulfur in the same apparatus under the same conditions of temperature and pressure never yielded more than a very faint browning of the lead acetate paper. In no case was a blackening of the test paper produced. If the hydrogenated element was placed in the apparatus, Fig. 1, without sulfur, the lead acetate paper remained white, showing that impurities did not cause the results about to be described.

Cathodically hydrogenated palladium, nickel, silicon, Acheson graphite or coconut charcoal when placed in the apparatus, Fig. 1, at temperatures of 93 to 99° always caused a blackening of the lead acetate paper. At temperatures ranging from 65 to 93°, a distinct browning of the test paper was observed. Below 65° the test paper showed no visible change. In all of these experiments, however, it was clearly evident that only a small fraction of the total quantity of the hydrogen liberated from any of the cathodically hydrogenated elements mentioned exercised this reducing action on roll sulfur. Moreover, this chemical action was not strong until after about five minutes had elapsed, indicating that the bulk of the hydrogen which was superficially held or easily liberated was practically inactive as compared with the more reluctantly released smaller portion of the hydrogen.

Summary

1. Practically all metals when heated in hydrogen, nitrogen, helium, argon, carbon dioxide or oxygen give off a peculiar, disagreeable, burnt nitrogenous odor which is due to impurities gathered on their surfaces from the air or objects with which they have been in contact. These impurities are dust particles laden with microorganisms, and the odor observed on heating is due to decomposition of the latter. When oxygen is used, the odor is slight and soon disappears, because complete oxidation to odorless products ensues. The presence of carbon in the odoriferous gas was established chemically. Hydrogen sulfide is also present in the gas, and the lead acetate test for it is positive as long as the odor lasts and for a very considerable time after the odor is gone.

2. When the metals are heated in hydrogen until all odor and hydrogen sulfide have disappeared, the hydrogen is unable to give hydrogen sulfide tests when passed over sulfur, or to reduce permanganate, ferric salts or blue starch iodide paper. The sulfur comes from sulfur compounds adsorbed by the metals from the air. Silver is especially able to take on sulfur.

3. Hydrogen passed over very pure hot silver was subjected to special study, chemically and spectroscopically. By this latter method it could not be distinguished from ordinary pure hydrogen. Observations were made in the visible and also in the ultraviolet. Quartz spectrograph and quartz vacuum tubes were employed in the latter case.

The hydrogen reduced permanganate, ferric chloride, blue starch iodide and yielded positive tests for hydrogen sulfide on the lead acetate paper as long as the odor persisted. The reductions also continued as long as did the hydrogen sulfide test, but no longer. The gas after that also gave no hydrogen sulfide test when passed over sulfur, even when the latter was at 65°.

The silver when cooled and kept in pure hydrogen, and then later heated again, never produced either the odor, the hydrogen sulfide test, or the reducing reactions. However, even momentary exposure to ordinary air at once resulted in the odor, the hydrogen sulfide test and the "activation."

4. Hydrogen released from cathodically hydrogenated Pd, Ni, Si or C in the form of Acheson graphite or coconut charcoal was found to be chemically active in that it reduced sulfur above 65°. Only a small fraction, namely, the more tightly held portion of the hydrogen, was found to be thus active.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

The Activities of Ethylene and Ethanol in Sulfuric Acid

BY M. GALLAGHER AND D. B. KEYES

The purpose of this investigation was primarily to determine the activity of ethylene in concentrated sulfuric acid and the activity of ethanol in dilute sulfuric acid. These activities are involved in the calculation of the free energy change taking place in the formation of ethanol from ethylene and water by means of the reactions

$$C_2H_4(g) + H_2SO_4 = C_2H_5HSO_4 \quad (1)$$

$$C_2H_5HSO_4 + H_2O(l) = C_2H_5OH(l) + H_2SO_4 \quad (2)$$

whose sum is

$$C_2H_4(g) + H_2O(l) = C_2H_5OH(l) \quad (3)$$

An experimental value for the free energy from such equilibrium measurements is desirable in view of the discrepancies in the figures which have been published.

The values ΔF_{700} concern the reaction with all the compounds as gases; ΔF_{298} refer to the same reaction with ethanol and water as liquids.

The addition of reactions 1 and 2 seems more advisable than the direct hydration in reaction 3, since very small concentrations of alcohol are involved, the analysis of which is likely to result in large errors. Presuming the value of F_{700} = +14,070 calories published by Parks and Huffman to be correct, the conversion to ethanol would be only 0.005%, giving a concentration