same amount of acetylene initially charged, at identical fractions of active surface covered, and of course at different temperatures.

TABLE IV

SORPTION OF ACETYLENE BY SILVER NITRATE

Energy of activation

$$Ea = (2.303R)\frac{(T_1T_2)}{(T_1 - T_2)}\log\frac{(\text{Rate}_1)}{(\text{Rate}_2)}$$

| $t_1$ (Deg. C.) | $t_2$ (Deg. C.) | $(\text{Rate})_1 \times 10^3$ | $(\text{Rate})_2 \times 10^3$ | $E_a$, kcal./mole |
|---|---|---|---|---|
| | | $\left(\frac{\text{mole } C_2H_2}{\text{mole AgNO}_3}/\text{Min.}\right)$ | | |
| | | $\sigma = 0.200$ | | |
| 126.8 | 113.1 | 6.72 | 4.51 | 8.9 |
| 113.1 | 95.8 | 4.51 | 3.20 | 5.6 |
| 126.8 | 95.8 | 6.72 | 3.20 | 7.0 |
| | | $\sigma = 0.500$ | | |
| 126.8 | 113.1 | 5.20 | 32.4 | 10.6 |
| 113.1 | 95.8 | 3.24 | 2.33 | 5.4 |
| 126.8 | 95.8 | 5.20 | 2.33 | 7.6 |

Comparison of rates at 96, 113 and 127° for surface coverages of $\sigma = 0.200$ and 0.500 show values which fall between 5 and 10 kcal./mole (Table IV). Although it is clear that the apparent energies of activation calculated in this way are not independent of temperature, it is worth noting the $E_a$ for any two temperatures is nearly independent of surface coverage up to $\sigma = 0.5$ and that its value is in the range below that expected for reaction. Unfortunately, the precision of measurement at $\sigma > 0.85$ and at the higher temperatures, where a much higher energy of activation is to be expected since oxidation begins at higher temperature, is insufficient to allow calculation of $E_a$. It will be observed, however, that the rate of sorption always falls sharply near $\sigma = 0.85$ and that, therefore, the energy of activation is evidently much greater than 10 kcal./mole in this range.

From the previous discussion of results at the three lower temperatures, it will be recalled that attempts to measure the rate of desorption showed it to be immeasurably slow and therefore strongly indicative of a very large activation energy for desorption, as well as a high heat of sorption.

Beeck[5] also reported high heats of sorption together with low energies of activation for hydrogen sorbed on metals.

(5) O. Beeck, "Advances in Catalysis," Vol. II, Academic Press, Inc., New York, N. Y., 1950, p. 193.

PHILADELPHIA, PENNSYLVANIA

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[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

# The Mechanism of Acetylene Oxidation by Supported Silver Nitrate[1]

BY W. T. M. JOHNSON AND K. A. KRIEGER

RECEIVED APRIL 19, 1954

The reaction between acetylene and silver nitrate has been studied using carbon-14 from 125 to 200°. The technique allowed observation of separate sorption and oxidation steps. At 125° only sorption occurs; above 149° sorption and oxidation occur producing carbon dioxide. The unusual feature of this process is that a critical amount of sorption is required for oxidation. Carbon dioxide evolution is delayed until after the sorption of a definite amount of acetylene. The amount of sorption required to initiate oxidation decreases with increasing temperature. The reaction is partly a stoichiometric reaction between acetylene and silver nitrate. It is suggested that polymerization of acetylene occurs on the silver nitrate surface whenever adjacent acetylene sorption occurs, and that these "polyacetylenes" are oxidized by the silver nitrate to carbon dioxide. The amount of sorption is critical because adjacent site sorption (prerequisite for surface polymerization) is prevented at lower amounts of sorption by (a) intermolecular repulsive forces or (b), the variation in activity over the catalyst surface, which makes improbable adjacent sites of equal activity. This study allows no decision between (a) and (b).

This work originated from a study of catalysts for the oxidation of acetylene in air[2] and was intended to be a kinetic study. However, when preliminary runs disclosed the rather unusual nature of the oxidation, our attention was shifted to a study of the nature of this reaction. Carbon-14 labeled acetylene was used as an analytical tool permitting operation at low acetylene concentrations and high space velocities. This technique had the unique advantage of allowing rather detailed observation of the separate sorption and oxidation processes occurring in the acetylene reaction. From this study, a reaction behavior has been uncovered which we do not believe has been reported previously.

## Experimental

**Materials.**—The preparation of acetylene-air mixtures and of the catalyst used in these runs has been described.[2] Labeled acetylene was prepared from two millicuries of carbon-14 as barium carbonate obtained from the U. S. Atomic Energy Commission following the procedure of Maquenne.[3] The yield was 65% calculated on barium carbonate. The acetylene–air mixtures were passed into the catalytic apparatus through Ascarite and Drierite.

The oxygen-free nitrogen was prepared from cylinder nitrogen by passage over hot copper turnings, previously reduced in hydrogen.

Geiger counters were assembled from Radiation Counter Laboratory Pressure Seal Mica Window Counter Kits using a special clamping ring for attachment to a spherical glass gas-cell and were filled with a mixture of 90% neon and 10% ethanol to a total pressure of 110 mm. Two such gas-cell counters were constructed with plateaus of 160-200 volts. Mica window thicknesses were 3.4 and 3.9 mg./cm.[2]

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(1) This work was carried out in the Thermodynamics Research Laboratory of the University of Pennsylvania and was supported by the Navy Department, Bureau of Ships. The material for this paper was taken from the Ph.D. thesis of W. T. M. Johnson, 1950, and was presented in part at Chemistry Conference No. 4, Brookhaven National Laboratory, 1950, and at the Chicago Meeting of the A.C.S., September, 1953.

(2) K. A. Krieger, THIS JOURNAL, **71**, 3156 (1949).

(3) L. Maquenne, *Bull. soc. chim.*, **8**, 773 (1892).

**Apparatus and Procedures.**—A conventional flow system was modified to allow practically continuous analysis of gaseous radioactive products. Outlet gases from the catalyst chamber passed into a system of three alternate paths leading into the Geiger counter gas cell. This arrangement permitted determination of acetylene, carbon dioxide and carbon monoxide. A glass tube, path A, enabled measurement of total C-14 in gaseous products. Path B led through an Ascarite bulb, removing carbon dioxide, and giving the amounts of acetylene plus carbon monoxide. Path C, a packed liquid air trap, passed only carbon monoxide. An Emil Greiner Cartesian Manostat was used to maintain constant pressure in the system. Gas samples for colorimetric acetylene determination were taken at the outlet from the gas cell. The exhaust gases were passed through ammoniacal silver nitrate to absorb residual carbon dioxide and acetylene and then into the hood exhaust. A General Radio Company Counting Rate Meter was used to measure the activity of the flowing gases and the results were traced on a Leeds and Northrup Speedomax G Recorder. The catalyst bed temperature was controlled to ±0.5° except as noted, using a Thyratron thermoregulator. Runs were made at pressures of 400 mm. and with contact times of about 0.1 second.

**Analytical.**—Procedures used here for the colorimetric analysis of acetylene have been described.[4] The recorder charts of the product gas activities were used to estimate gas concentrations. By alternating the gas flow among the three paths, a series of traces representing the counting rates for the gases sought were obtained. Corresponding traces were connected and curves representing the concentration of each labeled gas as a function of time were obtained. The background was obtained by passing dry air through the counter cell before and after each run, under the run conditions, and was subtracted from the total activities. Most of the uncertainty of the radioactive analyses was due to background variation during the run. The activity of the inlet acetylene was measured before and after each run at the same time samples were taken for chemical analysis. This procedure identified the inlet acetylene concentration with the inlet acetylene counting rate. The usual reproducibility of inlet activities (before and after runs) was ±2%. Differences between chemical and radioactive analyses were usually less than ±5%, although a few larger differences (up to ±15%) were found. The differences found were non-systematic and did not affect the nature of the conclusions.

X-Ray studies of the catalysts were made with a Norelco recording X-ray spectrometer using Cu K$\alpha$ radiation.

The silver acetylide–silver nitrate complex, used for X-ray comparison with the surface complex found, was prepared by bubbling purified acetylene into aqueous silver nitrate solution. Analysis of this material gave 78.66 ± 0.04% silver which compares with the calculated value of 78.98%.

## Results and Discussion

The oxidation of acetylene over supported silver nitrate was studied at 125, 149, 170 and at 200° at a total pressure of 400 mm. The acetylene concentration was 0.11% in air and the reaction time 0.1 second. The catalyst used was No. 192 described by Krieger.[2] The courses of the reactions are shown in the following graphs and the data are given in Table I.

TABLE I

ACETYLENE OXIDATION IN AIR

| Temp., °C. | Time to $CO_2$ appearance, min. | $C_2H_2$ sorbed,[a] moles per mole $AgNO_3$ | Composition[b] of spent catalyst |
|---|---|---|---|
| 125 | No $CO_2$ found[c] | 0.33 | Alumina |
| 149 | 85 | .27 | Alumina and silver |
| 170 | 20 | .22 | Alumina and silver |
| 200 | 2 | .03 | Alumina and silver |

[a] Acetylene sorbed up to the minimum in the acetylene curve. [b] Determined by X-ray diffraction pattern. [c] No carbon dioxide was evolved up to 210 minutes.

The features of the reaction at 149° (Fig. 1) are an initially complete acetylene sorption which declines rapidly to a minimum then increases to a maximum. Carbon dioxide evolution does not begin until after the minimum in the acetylene sorption curve has been passed. The temperature in the catalyst bed shows a large and significant rise at 90 minutes, nearly coincident with the start of carbon dioxide evolution. From this curve, it was found that 0.27 mole of acetylene were sorbed per mole of silver nitrate up to the minimum in the acetylene removal curve. The used catalyst was black and contained metallic silver, in contrast to the white fresh catalyst.

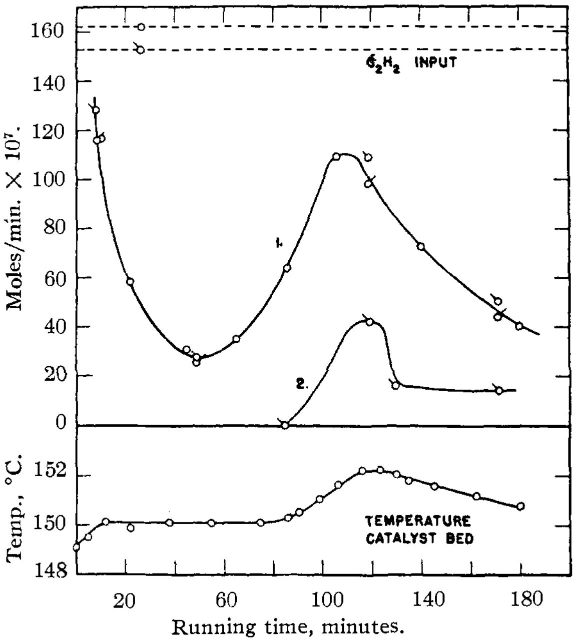

Fig. 1.—Acetylene oxidation at 149°: 1, acetylene taken up; 2, carbon dioxide output; o, ȯ, colorimetric; ƀ, radioactive.

At 200° the reaction follows a different course (Fig. 2). The acetylene removal is nearly complete for 60 minutes, then declines. Carbon dioxide evolution begins near the start of the run and is again coincident with a large rise in temperature in the catalyst bed. In the brief period preceding carbon dioxide evolution, an estimated 0.03 mole of acetylene was sorbed per mole of silver nitrate. The spent catalyst contained metallic silver.

The course of the reaction at 170° is clearly intermediate to the reactions at 149 and 200° (Fig. 3). The minimum in the acetylene curve comes after 20 minutes, and, as before, signals the start of carbon dioxide evolution and the large rise in temperature in the catalyst bed. In this case, the catalyst sorbed 0.22 mole of acetylene per mole silver nitrate before the start of carbon dioxide evolution, and again metallic silver was found on the spent catalyst.

These results suggested that little oxidation should occur at temperatures much below 140° and the experiment at 125° showed that this is the case (Fig. 4). There was no carbon dioxide evolution, no large rise in temperature in the catalyst

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(4) T. A. Geissman, S. Kaufman and D. Y. Dollman, *Ind. Eng. Chem., Anal. Ed.*, **19**, 919 (1947).

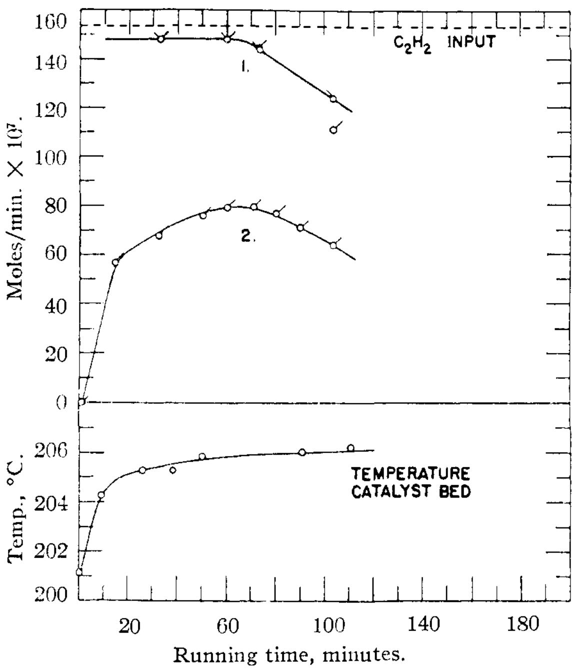

Fig. 2.—Acetylene oxidation at 200°: 1, acetylene taken up; 2, carbon dioxide output; ƀ, colorimetric; ♂, radioactive.

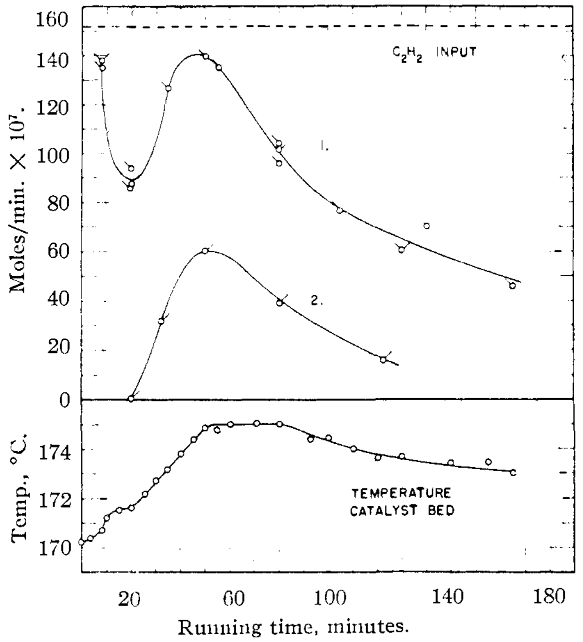

Fig. 3.—Acetylene oxidation at 170°: 1, acetylene taken up; 2, carbon dioxide output; ƀ, colorimetric; ♂, radioactive.

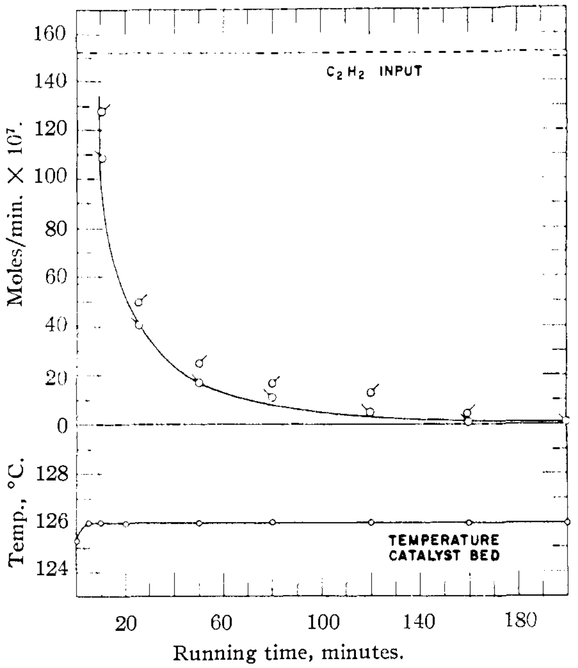

Fig. 4.—Acetylene oxidation at 125°: acetylene taken up (no carbon dioxide evolved); ƀ, colorimetric; ♂, radioactive.

bed, and the acetylene curve did not show a maximum. There was 0.33 mole of acetylene sorbed per mole of silver nitrate, and no metallic silver was detected on the spent catalyst.

These findings suggest that acetylene is sorbed and subsequently oxidized in separate processes and that the duration of the sorption process depends on the temperature. The time to complete the sorption step decreases with increasing temperature, and carbon dioxide evolution occurs after smaller amounts of acetylene are sorbed. The coincidence of the large increase in temperature in the catalyst bed and the appearance of carbon dioxide in the product gases suggests that the rise in temperature occurs as a result of the oxidation of sorbed acetylene to carbon dioxide.

**Delayed Oxidation.**—The unusual feature of this reaction is the delay in the oxidation of the sorbed acetylene. One would expect some oxidation to occur shortly after acetylene sorption at temperatures capable of supporting oxidation, and consequently it is essential to demonstrate that the delayed appearance of carbon dioxide is actually a result of delayed *oxidation* and not of some secondary process. An apparent delay could result from down-stream sorption of carbon dioxide, which would prevent the appearance of carbon dioxide in the off-gas until the catalyst was saturated with carbon dioxide.

Two experimental observations make this possibility seem remote. The first is the well-defined agreement between the rise in temperature in the catalyst bed and the appearance of carbon dioxide. This correlation was noted at all temperatures. The second observation was that saturation of the catalyst with unlabeled carbon dioxide prior to the run had little effect on the course of the reaction. In this test an excess of dry unlabeled carbon dioxide was placed in contact with the catalyst at the reaction temperature for two hours before the run. The results showed that the course of the reaction was essentially unchanged (Fig. 5). Down-stream sorption of carbon dioxide would have been indicated by the evolution of carbon dioxide immediately or after a shorter time than in the reaction in which carbon dioxide was not previously added.

Similar experiments with carbon monoxide resulted in a complete poisoning of the catalyst. Very little acetylene was sorbed, neither carbon

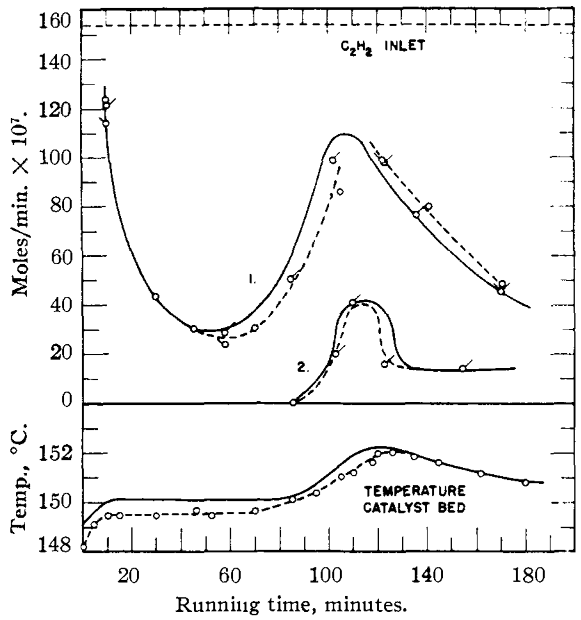

Fig. 5.—Carbon dioxide poisoning, 149°: 1, acetylene taken up; 2, carbon dioxide output; solid line, unpoisoned surface; o, ƀ, colorimetric; ơ, radioactive.

dioxide nor carbon monoxide was evolved, and the characteristic rise in temperature in the catalyst bed did not occur. The spent catalyst showed the presence of metallic silver indicating the reduction of silver nitrate by the carbon monoxide. Since the heats of combustion of acetylene to carbon dioxide and to carbon monoxide are not very different (310 and 240 kcal./mole, respectively), carbon monoxide, if formed at all, must be a short-lived intermediate, or two temperature rises rather than one would have been observed. These tests support the idea that there is an actual delay in the oxidation of acetylene and not merely a delay in the evolution of products from the catalyst surface.

**Experiments under Varied Conditions.**—Certain other experiments throw additional light on the course of the over-all reaction. Runs at a higher oxygen pressure (130 mm.) at 149° showed that the amount of sorption before reaction does not depend on oxygen pressure over this range. The reaction showed the same behavior as at the lower oxygen pressure (80 mm.). The amount of acetylene sorbed was 0.29 mole per mole of silver nitrate (*cf.* Table I). This indicates that oxygen is not involved in the step which is the precursor of oxidation.

The reaction of acetylene–nitrogen mixtures over the silver nitrate catalyst was studied at 152° and at 200° (Figs. 6 and 7). These experiments showed the reaction behavior to be very similar to the reaction in the presence of oxygen. Apparently the oxygen appearing in the carbon dioxide comes partly from the silver nitrate. However, since 3–4 times as much carbon dioxide is formed in the presence of air, it was concluded that the reaction in air is partly catalytic. Possibly oxygen may act to regenerate the silver salt catalyst.

An attempt was made to observe the state of the silver nitrate catalyst during the reaction near 150° by means of X-ray studies. This procedure gave evidence for the formation of a surface complex resulting from the reaction of acetylene and silver nitrate. In separate runs, the reaction was carried out for 50, 70, 130 and 210 minutes, covering the previously determined maxima and minima in the acetylene curve at this temperature. After these times, the catalyst was immediately removed and X-rayed. The results (Fig. 8) show the rapid disappearance of silver nitrate during the acetylene sorption process, the formation and decline of a surface complex, and lastly, the appearance of metallic silver. The surface complex was tentatively identified as $Ag_2C_2 \cdot AgNO_3$ by comparison with the X-ray spectra of synthetic silver acetylide–silver nitrate.

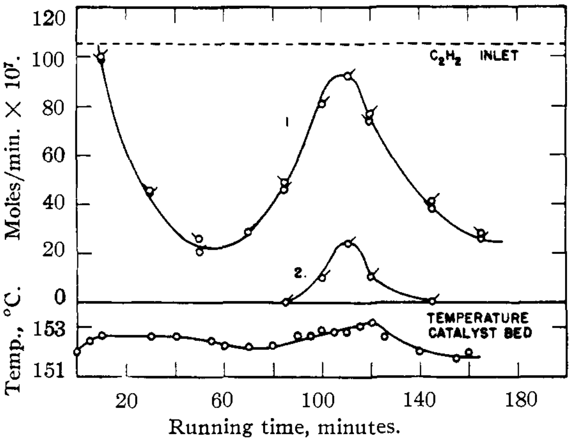

Fig. 6.—Acetylene–silver nitrate reaction at 152°: 1, acetylene taken up; 2, carbon dioxide evolved; ƀ, colorimetric; ơ, radioactive.

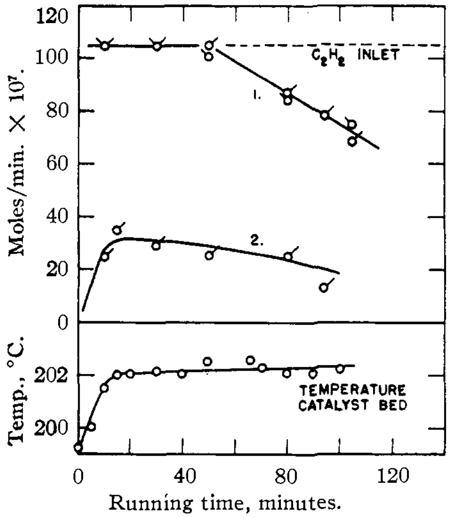

Fig. 7.—Acetylene–silver nitrate reaction at 200°: 1, acetylene taken up; 2, carbon dioxide evolved; ƀ, colorimetric; ơ, radioactive.

**Proposed Mechanism.**—If a critical concentration of acetylene on the catalyst surface is necessary for reaction to proceed, then this physical clustering of acetylene must somehow enhance the possibility of reaction. We suggest that the sorption of a critical amount of acetylene favors reaction by allowing interaction between sorbed acetylene

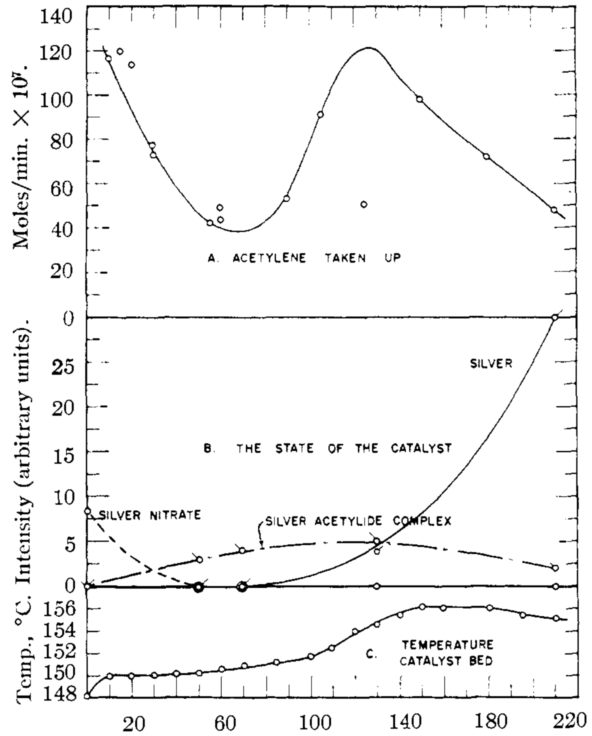

Fig. 8.—Catalyst behavior during run: A, acetylene taken up; B, state of catalyst; C, temperature catalyst bed.

molecules. This interaction leads, then, to a kind of surface polymerization of acetylene forming polyacetylenes, probably diacetylenes, more easily oxidized than acetylene itself. To explain why this polymerization does not occur at lower surface coverages, it is necessary to assume either (a) that adjacent site sorption is prevented by intermolecular repulsion between sorbed acetylene molecules or (b) that sorption takes place on nonadjacent sites because the variation in activity over the catalyst surface is such that highly active centers infrequently occur in adjacent positions.

According to the proposed mechanism, nearest neighbors occur only when surface coverage reaches a value such that next sorbed acetylene molecules condense on sites adjacent to occupied sites. Carbon dioxide formation from such a reaction would not increase with $\theta$ or $(1 - \theta)$ but would remain zero until a critical value of $\theta$ was reached, then increase rapidly. The effect of temperature on such a reaction would be in qualitative agreement with our findings. With increasing temperature bimolecular surface reactions forming polyacetylenes would occur at smaller values of $\theta$ because the increased thermal energy of the sorbed acetylene molecules would tend to overcome intermolecular repulsive forces; and to permit activated migration to sites of lower activity. Such behavior would appear experimentally as a decrease in the amount of sorption preceding reaction with increasing temperature. Table II lists the surface coverage by acetylene prior to reaction as a function of temperature.

Completing the postulated reaction mechanism we suggest that the polymerization of sorbed acetylene makes oxidation possible because the polyacetylenes are more readily oxidized than acetylene. At lower temperatures sorption may also lead to the critically initiated surface polymerization, but no oxidation occurs because the temperature is too low.

Table II

Surface Coverage Preceding Reaction ($\theta_r$)

| Temp., °C. | $\theta_r$[a] |
|---|---|
| 149 | 0.80 |
| 170 | .65 |
| 200 | .1 |

[a] Computed from the amount of sorption at 125° (where no reaction occurs) as a measure of the total surface available to acetylene.

The reaction mechanism postulated is then in summary:

Acetylene Oxidation

$$mC_2H_2\,(\text{gas}) \xrightarrow[\text{AgNO}_3]{} (C_2H_2)_n\ \text{sorbed} \xrightarrow[\text{AgNO}_3]{} CO_2 + H_2O + AgNO_x\ (x < 3)$$

Catalyst regeneration (in air)

$$AgNO_x + O_2 \longrightarrow AgNO_3$$

Catalyst decomposition

$$AgNO_3 \longrightarrow Ag + \text{oxides of nitrogen}$$
$$AgNO_x \longrightarrow Ag + \text{oxides of nitrogen}$$

The main features of these experimental findings are supported by the work of Kirsch and Krieger[5] who found a critical amount of sorption necessary for reaction; sorption behavior suggesting surface acetylene polymerization; sorption at lower temperatures, reaction at higher; and a reaction between acetylene and silver nitrate in the absence of oxygen. Their work shows most strikingly the critical nature of the reaction—that the sorption of a small additional amount of acetylene on the silver nitrate surface precipitates reaction in an acetylene–silver nitrate system that has remained unreactive for long periods.

There is a small amount of data in the literature to support the idea of polyacetylene formation and oxidation under these conditions. A polymolecular reaction mechanism is supported by the finding that diacetylenes are formed from cuprous acetylides under mild oxidizing conditions[6] which is certainly a reasonable parallel to the present case. In addition, recent calculations by Longuet-Higgins and Burkitt[7] of force constants and bond lengths in polyacetylenes suggest that polyacetylenes should—because of greater triple bond lengths and smaller force constants—be more readily oxidized than acetylene.

Further experimental tests of this mechanism might involve (a) comparison of the ease of oxidation of acetylene with that of diacetylene or (b) infrared examination of acetylene sorbed on silver nitrate as a function of surface coverage.

It is quite possible that phenomena of this kind occur in other reactions, but are not commonly observed because the experimental conditions are not appropriate. We believe that the low acety-

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(5) F. W. Kirsch and K. A. Krieger, This Journal, **76**, 4778 (1954).

(6) F. Straus and L. Kollek, *Ber.*, **59B**, 1664 (1926).

(7) H. C. Longuet-Higgins and F. H. Burkitt, *Trans. Faraday Soc.*, **48**, 1077 (1952).

lene concentrations and short contact times used in these studies, together with an analytical method yielding virtually continuous analyses, have made it possible to observe the conditions which obtain during the *formation* of the reactive surface layer; whereas the usual experimental procedures observe only the steady state conditions.

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[CONTRIBUTION FROM DEPARTMENT OF METALLURGY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

# Thermal Dissociation of Sulfur Dioxide and the Dissociation Energy of SO and $S_2$

BY GEORGE ST. PIERRE AND JOHN CHIPMAN

RECEIVED MARCH 10, 1954

The ratio $j = Fe^{+++}/(Fe^{+++} + Fe^{++})$ in lime–iron oxide slags in equilibrium with $SO_2$ or $SO_2$-CO mixtures is used to determine the partial pressure of $O_2$ in the gas at 1550°. The products of dissociation of $SO_2$ at this temperature are principally SO and $O_2$. The data lead to a decision between possible values for the dissociation energies of SO and $S_2$ in favor of 5.146 and 3.6 e.v., respectively. The free energy of formation of SO from $S_2$ and $O_2$ at 298.16 and 1823°K., respectively, is −18.6 and −20.6 kcal./mole.

## Introduction

TABLE I

SUMMARY OF THERMODYNAMIC PROPERTIES AT 1823°K.

| | S | O | $S_2$[a] | $O_2$ | SO[a] | $SO_2$[a] | CO | $CO_2$ | COS[b] | $SO_3$[a] |
|---|---|---|---|---|---|---|---|---|---|---|
| $-(F° - E°_0)/T$ | 44.453 | 42.539 | 61.66 | 55.369 | 59.82 | 69.20 | 53.369 | 60.76 | 65.75 | 75.53 |
| $(H° - E°_0)/T$ | 5.222 | 5.080 | 8.49 | 8.025 | 8.21 | 12.01 | 7.739 | 11.84 | 12.36 | 17.62 |
| $S^0$ | 49.675 | 47.620 | 70.15 | 63.394 | 68.03 | 81.21 | 61.108 | 72.60 | 78.11 | 93.15 |

[a] Extrapolated from 1500°K. using $C_p$ data. [b] Extrapolated from 1800°K. using $C_p$ data.

The dissociation products of sulfur dioxide at high temperatures include $S_2$, $O_2$, SO, $SO_3$, S and O. Equilibrium concentrations under given conditions are unknown because of major uncertainties in the heats of formation of $S_2$ and SO from the atoms. The importance of these gases in many pyrometallurgical processes, in particular their reactions with slags containing oxygen and sulfur, has led to this study. Data will be presented which establish the oxygen pressure at 1550° in pure $SO_2$ and in several $SO_2$–CO mixtures which lead to a clear choice among the proposed values for the uncertain heats of formation.

**Spectroscopic and Thermochemical Data.**—Data on the thermodynamic properties of all the gases under consideration are presented in Table I. The data for each gas except COS have been taken from "Selected Values of Chemical Thermodynamic Properties."[1] The values for COS are those given by Cross.[2]

In Table II are summarized data on some heats of formation.

The several heats of formation of SO and $S_2$ from the atoms arising from different interpretations of the spectroscopic measurements are reported. According to Gaydon,[3] if the predissociation limit of 41,520 cm.$^{-1}$ for SO is due to a $^3\pi$ state arising from normal atoms, then the dissociation energy is 5.146 e.v.; however, if it goes to O($^3P$) and S($^1D$) then the dissociation energy is 4.002 e.v. Gaydon favored the first interpretation while Herzberg[4] chose the latter. The situation for $S_2$ is similarly uncertain and it appears that the two values for SO and the three values for $S_2$ are equally probable. Six different values for the heat of formation of SO from $S_2$ and $O_2$ are given in Table III.

TABLE II

SUMMARY OF DATA ON HEATS OF FORMATION

| Reaction | $\Delta H°_0$ E.v./mole | $\Delta H°_0$ Kcal./mole | $\Delta H°_{298.16}$, kcal./mole | Method of determ. | Reference |
|---|---|---|---|---|---|
| S + O = SO | −4.002 | − 92.3 | | Spect. | a,b,c |
| | −5.146 | −118.7 | | | |
| $2S = S_2$ | −3.3 | − 76 | | | |
| | −3.6 | − 83 | | Spect. | a,b,d,e,p |
| | −4.4 | −101 | | | |
| $2O = O_2$ | −5.115 | −117.96 | | Spect. | a,b,n |
| $1/2S_2 + O_2 = SO_2$ | | − 85.74 | −86.36 | Calor.<br>Equil. | f,g,h,i<br>j,k,l,o |
| $CO + 1/2O_2 = CO_2$ | | − 66.767 | −67.636 | Calor. | f |
| $CO + 1/2S_2 = COS$ | | − 21.01 | −21.78 | Calor.<br>Equil. | f,m |
| $SO_2 + 1/2O_2 = SO_3$ | | − 22.70 | −23.47 | Calor. | f |

[a] A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," John Wiley and Sons, Inc., New York, N. Y., 1947. [b] G. Herzberg, "Molecular Spectra and Molecular Structure. I. Diatomic Molecules," 1st Ed., Prentice-Hall Inc., Co., New York, N. Y., 1939; 2nd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1950. [c] E. V. Martin, *Phys. Rev.*, **41**, 167 (1932). [d] E. Olsson, *Z. Physik*, **100**, 656 (1936). [e] G. M. Naude and A. Christy, *Phys. Rev.*, **37**, 490 (1931). [f] "Selected Values of Chem. Therm. Prop., Circ. 500," Natl. Bur. Std., 1952. [g] E. D. Eastman, *Bur. Mines Inform. Circ.*, **6454** (1931). [h] J. R. Eckman and F. D. Rossini, *J. Research Natl. Bur. Standards*, **3**, 597 (1929). [i] J. B. Ferguson, THIS JOURNAL, **40**, 1626 (1918); **41**, 69 (1919). [j] G. Preuner and W. Schupp, *Z. physik. Chem.*, **68**, 157 (1909). [k] A. R. Gordon, *J. Chem. Phys.*, **3**, 336 (1935). [l] K. K. Kelley, *U. S. Bur. of Mines Bull.*, **406** (1937). [m] E. Terres and H. Wesemann, *Angew. Chem.*, **45**, 795 (1932). [n] P. Bix and G. Herzberg, *J. Chem. Phys.*, **21**, 2240 (1953). [o] H. Braune, S. Peter and V. Nevelling, *Z. Naturforsch*, **6a**, 32 (1951). [p] P. Goldfinger, W. Jeunehomme and B. Rosen, *Nature*, **138**, 205 (1936). *Cf.* W. Nernst and H. von Wartenberg, *Z. Elektrochem.*, **9**, 626 (1903); *Z. anorg. Chem.*, **56**, 320 (1908).

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(1) "Selected Values of Chem. Therm. Prop.," Series III, Natl. Bur. of Std., Loose Leaf, 1947-1951.

(2) P. C. Cross, *J. Chem. Phys.*, **3**, 825 (1935).

(3) A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," John Wiley and Sons, Inc., N. Y., 1947. In a private communication Professor Gaydon states that the listed value, 5.184 e.v., should have read 5.148.

(4) G. Herzberg, "Molecular Spectra and Molecular Structure. I. Diatomic Molecules"; 1st Edn., Prentice-Hall Book Co., N. Y., 1939; 2nd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1950.