to a matter of definitions. We believe that it is appropriate and convenient to define, as we have done, the whole of the *increased* energy stabilization which results when hyperconjugation is taken into account as HCJE. (Similar problems of definition arise in some cases for ordinary conjugation or resonance, especially frequently where ions are concerned.)

Large shifts in ultraviolet N,V spectra on methylation are known, even for simple neutral molecules of the alternant hydrocarbon type, such as ethylene, butadiene and benzene, which can be accounted for by hyperconjugation[13a,18] using parameter values similar to those of the present paper. For the same molecules, methylation causes changes (decreases) of still larger magnitude in ionization potential. A fraction of the observed decrease can be accounted for[13a] by hyperconjugation in the ion without charge transfer (*i.e.*, assuming $\delta = 0$, $\omega = 0$). In view of the great increase in computed HCJE found in the present paper in the case of $C_6H_7^+$ when allowance is made for charge transfer, it seems likely that the remainder of the observed decreases in ionization potential on methylation could be accounted for in terms of hyperconjugation with charge transfer, using self-consistency procedures as in the present paper. Such computations, however, have not yet been made.

LAFAYETTE, INDIANA

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

Sorption of Acetylene by Silver Nitrate

BY F. W. KIRSCH AND K. A. KRIEGER

RECEIVED APRIL 19, 1954

Silver nitrate catalysts important in the low temperature oxidation of acetylene have been studied as they function in oxidation and in the chemisorption stage which is an essential precursor to oxidation. Primary emphasis was given to phenomena occurring below 130°, which is the maximum temperature at which sorption is not complicated by oxidaton. Measurement of sorption rates revealed an inverse relation between rate and acetylene pressure. This observation has been interpreted as an "autopoisoning" effect, which produces a layer of acetylene polymer resistant to penetration. Sorption rate can be correlated with the amount of free acetylene and of available surface, but regularly occurring discontinuities strongly suggest critical changes in the sorbent during sorption. Oxidation, with products identified as carbon dioxide, water, nitric oxide, nitrogen and possibly silver, proceeds at temperatures above 149° after a critical amount of acetylene sorption.

Introduction

A study of the low temperature oxidation of acetylene as catalyzed by silver nitrate supported on alumina revealed some steps in the process worthy of separate and more detailed research.[1] Foremost among these phenomena is the removal of acetylene from acetylene–air mixtures in a continuous process without a concomitant evolution of carbon dioxide in the product stream. This occurrence prompted efforts to clarify further the reaction mechanism with particular emphasis on the sorption step believed to be a prerequisite for oxidation.

In this study the sorption of acetylene on pure silver nitrate at temperatures between 96 and 170° was investigated in a closed system without gaseous oxygen. Preliminary tests having shown acetylene sorption by alumina to be immeasurably slow below 200°, the method of this research offered a somewhat simplified scheme for elucidating the sorption mechanism. Rates of sorption were measured in the lower temperature range; and, although oxidation complicates the picture somewhat at higher temperatures, it was found possible to elicit additional information on the sorption process.

Experimental

A. **Materials.**—The silver nitrate was prepared from C.P. grade salt by grinding and sizing through 200-mesh silk screens. At all times the sorbent was protected as much as possible from air and light before use.

Acetylene from commercial cylinders was passed successively through aqueous solutions of sodium bisulfite and sodium hydroxide and then dried before use.

B. **Analyses.**—Gas analyses were carried out with samples between 0.02 and 0.2 cc. (STP) by absorption in ammoniacal cuprous sulfate solution and measurement of acetylene by a colorimetric method.[2] For larger samples from experiments involving oxidation, CO_2, NO, C_2H_2 and CO were determined by differential absorption in standard reagents.

C. **Apparatus and Procedure.**—The apparatus used in this study was a constant volume, static system in which the sorption rates were quantitatively determined by following the decrease in gas pressure as a function of time.

Essentially the sorption system consisted of a furnace-enclosed Pyrex cylinder, to which a Zimmerli gage was attached. Pressures were read from the gage with a cathetometer. The sorption system proper, the product removal line, and the gas storage section were evacuated prior to sorption by an oil pump and a single-stage mercury diffusion pump, which produced a residual pressure of 4 to 9×10^{-6} mm.

Between the gas-storage section and the sorption system, a doser-bulb contained the acetylene before it was admitted for sorption.

Constant furnace temperatures were maintained by a Thyratron regulator within about ±0.25°, and sorption temperatures were determined by a Chromel-Alumel couple inserted in a thermowell extending from the outer end to the center of the sorption tube.

A sampling line, separated from the sorption section by a stopcock, contained a manually operated Töpler pump to assist in the removal of residual gas after completion of the process.

D. **Reversibility of Sorption and Attainment of Equilibrium.**—When excess acetylene was admitted to samples of silver nitrate which had been thoroughly out-gassed at pressures of the order of 9×10^{-6} mm., a rapid decrease in pressure occurred. Additional quantities of acetylene admitted subsequently experienced no decrease in pressure

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[1] W. T. M. Johnson and K. A. Krieger, THIS JOURNAL, **76**, 4782 (1954).

[2] T. A. Geissman, S. Kaufman and D. Y. Dollman, *Anal. Chem.*, **19**, 919 (1947).

over periods of approximately one hour. Even when the first admission of acetylene was followed by an out-gassing and heating period before the second portion of gas was admitted, no pressure decrease was observed. This behavior was common to the whole temperature range studied (94 to 170°).

Attempted measurement of desorption by a nearly instantaneous reduction in pressure to about 10^{-3} to 10^{-4} mm. and a subsequent observation of pressure in the sorption chamber failed to reveal the pressure increase which would be associated with a measurable rate of desorption.

In practice, equilibrium was considered to be attained if there was not a 0.1 mm. decrease in residual gas pressure in a 30-minute period. In several runs direct tests of this criterion were made by suddenly increasing acetylene pressure after apparent equilibrium had been reached and then observing the pressure during periods up to 1.5 hours. No further decrease in pressure was observed in these experiments.

E. **Reproducibility and Precision.**—Pressures were read to the nearest 0.05 mm. and are believed to be in error by no more than 0.1 mm.

Total sorption of acetylene was reproducible within about 1% at the higher temperatures and about 3% at the lower. Occasional larger errors were traced to leaks not detected at the beginning of the run.

Rates of sorption in check runs with the same initial pressures are reproducible to about 1% at the beginning of the run, but the uncertainty increases to about 10% as sorption nears completion.

Results and Discussion

A. **Sorption without Reaction.**—Analysis of the residual gas from sorption experiments at 127° and at 94.4° revealed that acetylene is the only component detectable in the gas phase in this temperature range. These experiments are uncomplicated by the occurrence of oxidation and give, therefore, quantitative measurements of rates of sorption.

Theoretical considerations predicted that the rate of sorption would vary directly with the acetylene pressure and the amount of free surface available; and the rate of sorption was plotted as a function of the amount of gas present (n) and the free surface ($1 - \sigma$). Rates were determined graphically by drawing tangents to the curve expressing the amount of gas as a function of time (Fig. 1). The fraction of the surface covered was calculated in terms of the surface available to acetylene at a particular temperature and not in relation to any measure of total surface.

Table I presents, in condensed form, the conditions and the results of sorption experiments at 96, 113 and 127°, in which only sorption is involved.

TABLE I

SORPTION OF ACETYLENE BY SILVER NITRATE WITHOUT OXIDATION

Temp., °C.	Gas pressure, mm. Initial	Gas pressure, mm. Final	Acetylene, mole × 10^5 Initial	Acetylene, mole × 10^5 Final	$\frac{(C_2H_2 \text{ taken up})}{(AgNO_3 \text{ charged})}$, molar ratio
127	11.9	8.5	15.58	11.51	0.118
127	12.6	9.1	16.38	12.24	.120
127	6.8	3.7	9.82	5.61	.120
127	7.0	3.9	10.12	5.88	.119
113	11.8	8.8	15.97	12.06	.111
113	10.9	7.9	14.88	10.88	.113
113	5.9	3.2	8.96	5.12	.109
113	6.0	3.1	9.05	4.98	.115
96	11.6	8.9	15.85	12.27	.102
96	11.6	9.0	15.85	12.41	.098
96	6.5	3.9	9.46	5.75	.105
96	6.4	3.8	9.30	5.60	.105

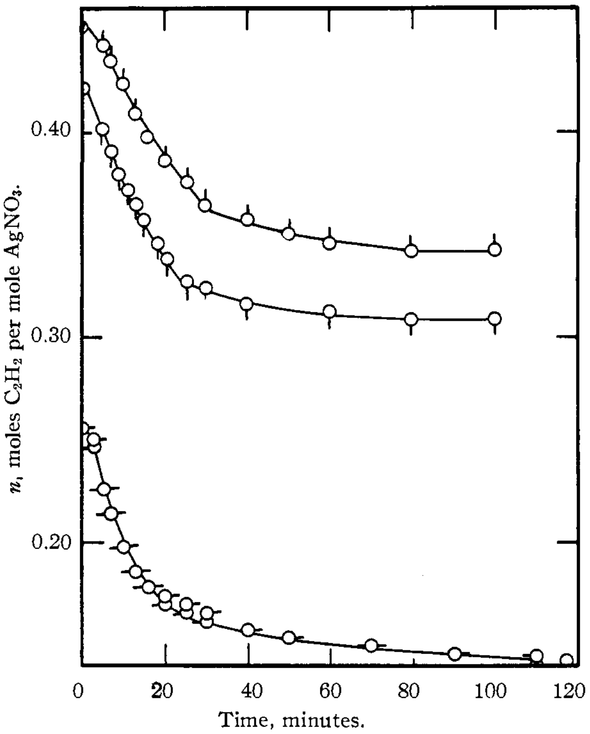

Fig. 1.—Sorption of acetylene by silver nitrate at 113°, amount of gas-phase acetylene (n) and time (t): ȯ, p_0 = 11.8 mm.; ọ, p_0 = 10.9; -o, p_0 = 5.9; o-, p_0 = 6.0.

Typical correlations of the rate data with the concentration of gas phase acetylene and the free surface are shown in Fig. 2.

Inspection of these data reveals three marked general observations: (1) the rate of acetylene sorption is linear in $n(1 - \sigma)$ over certain definite regions bounded by discontinuities in the lines; (2) the rate of sorption is an inverse function of initial pressure; and (3) the amount of acetylene sorbed is independent of pressure within the limits studied, but increases slightly with temperature.

A "break" is found in the curve when the sorbent is 30% saturated with acetylene. When the degree of coverage has reached a value of 80 to 85%, another "break" occurs and the rate is not linear in $n(1 - \sigma)$. For sorption at 127° an additional break near $\sigma = 0.5$ is evident.

Although rate measurements merely demonstrated the discontinuities without explaining them, it is possible that these "breaks" represent rearrangements of the sorbed layer which affect penetration of acetylene into the silver nitrate lattice, as well as the ease of oxidation of the sorbate under oxidizing conditions. A subsequent paper supports this concept.

In the case of sorptions carried out at various initial pressures, but at the same temperature, the "break" is far more prominent at low pressures than at high.

From a purely kinetic point of view, the second general observation named previously is mildly surprising. Increasing the total pressure of the sorbate would ordinarily be expected to increase the initial rate of sorption.

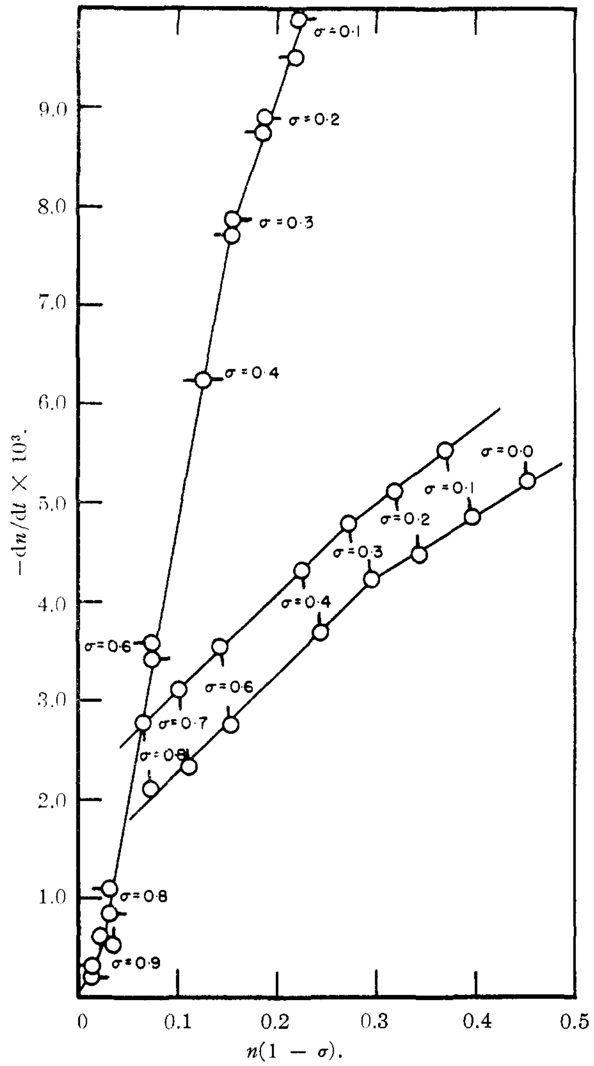

Fig. 2.—Sorption of acetylene by silver nitrate at 113°, rate of sorption ($-dn/dt$) correlated with gas-phase acetylene (n) and free surface ($1 - \sigma$): ò, p_0 = 11.8 mm.; ọ, p_0 = 10.9; -o, p_0 = 5.9; o-, p_0 = 6.0.

Approximate calculation of the geometric surface area of the silver nitrate shows that the amount of acetylene sorbed at saturation is about one thousand times that required to form a monolayer; it is, therefore, concluded that penetration of the solid does in fact occur.

From these considerations it is difficult to escape the conclusion that the relatively low chemisorption rate at high pressure is due to a change in character of the sorbate and possibly the sorbent. Cook and Oblad,[3] in studying the course of sorption as related to catalysis, have proposed that a surface may be strained and react more readily, "the adsorbate in effect creating the adsorption sites and thus reducing the strain upon the surface." Their so-called first-order strain has been described as the result of unbonded or distorted orbitals on crystalline surfaces of the catalyst. The phenomenon observed in this study can be explained if it is supposed that at relatively high pressure a dense population of acetylene molecules is produced and that interaction between sorbed molecules follows simultaneously with changes in the degree of solid strain. The interaction may be thought of as a polymerization which inhibits further penetration of the lattice. Lower initial pressures would then be expected to promote this interaction to a lesser degree.

The corresponding situation in the case of reaction on a surface is that of retardation of reaction rate by products of the reaction. Many such cases have been described: for example, Hinshelwood[4] reports this phenomenon to occur in the decomposition of N_2O on platinum.

In the temperature range of 96 to 127° the amount of acetylene taken up is independent of initial acetylene pressure, within experimental error. It is interesting to note that the equilibrium amount of acetylene held by the sorbent increases slightly with temperature For a reversible sorption the opposite effect would be expected because the kinetic energy of the sorbed molecules is greater. Sorption increasing with temperature suggests that at least some of the acetylene disappears from the gas phase by penetration of the silver nitrate lattice.

Attendant to the strength of the sorbed bond is the possibility that some nitrogen pentoxide and water vapor would be released during sorption. Products condensable in a trap surrounded by an isopropyl alcohol–Dry Ice mixture were found present in amounts between 5 and 10 micromoles. Lower oxides of nitrogen would have been accompanied by oxidation products of acetylene in the gas phase, which were never found at or below 127°. Over a period of time, a yellow substance was discovered in the trap after these lower temperature experiments, which, like mercuric oxide, turned red on heating before decomposing to mercury. The condensable vapors must, therefore, have been nitrogen pentoxide and water. The presence of these gases did not interfere with sorption measurements, since the freezing trap was always inserted between the sorption tube and the Zimmerli gage used for pressure measurement.

Estimation of the gas collision rate with the sorbent and comparison of this result with experimentally measured rates of sorption revealed a ratio of actual to calculated rates of 1.6×10^{-7} at 96°. This small collision efficiency suggests that there is something unusual about the surface of the solid which inhibits further sorption of acetylene.

B. Sorption and Reaction.—At 149° and higher temperatures, acetylene was found to react with silver nitrate in a manner significantly different from that described for lower temperatures. From this study it is possible to attribute the principal difference to acetylene oxidation, even though no free oxygen was initially present.

Table II summarizes the experimental conditions and results.

Runs made at 170° revealed a rapid pressure decrease relative to that occurring without oxida-

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[3] M. A. Cook and A. G. Oblad, *Ind. Eng. Chem.*, **45**, 1456 (1953).

[4] C. N. Hinshelwood, "The Kinetics of Chemical Change," Oxford University Press, London, 1940, p. 197.

TABLE II

SORPTION OF ACETYLENE BY SILVER NITRATE WITH OXIDATION

Temp., °C.	Gas pressure, mm.		Silver nitrate, initial (mole × 10^5)	Acetylene, mole × 10^5		Residual gas, mole × 10^5	$\frac{(C_2H_2 \text{ taken up})}{(AgNO_3 \text{ charged})}$, molar ratio
	Initial	Final		Initial	Final		
170	13.3	6.1	35.4	16.24	3.94	7.99	0.348
170	13.2	6.2	35.4	16.31	3.99	8.11	.349
149	12.6	7.5	35.4	16.00	8.67	9.96	.208
149	12.5	7.2	35.3	15.88	7.99	9.61	.224
149	13.0	7.6	35.3	16.44	8.57	10.19	.224

tion. Colorimetric analysis of the residual gas showed that it was not all acetylene, and it is therefore impossible to measure rates of sorption by the technique used in this study. It is possible, however, to investigate the mechanism of sorption and reaction and to determine, by correction for the presence of oxidation products, the equilibrium amount of acetylene taken up as 0.348 mole C_2H_2 per mole $AgNO_3$ at 170°, a value roughly three times as large as that without oxidation.

This result is explainable on the basis of results of another study which provides evidence that the sorbed polymerized acetylene layer is oxidized at this temperature. The greater total sorption and the faster rate are thus the consequences of the removal of the inhibiting layer of polymer.

Sorption at 149° had the characteristics of sorption plus oxidation. The apparent rate was slower than that at 170° and a smaller amount of acetylene was used up: 0.218 mole C_2H_2 per mole $AgNO_3$.

The spent silver nitrate was black and was inert to additional acetylene after sorption under these conditions (149 and 170°).

Analysis of the residual gas from sorption at 149° showed the presence of CO_2 in an amount roughly equivalent on a molar basis to the sum of the NO and N_2, which were present in almost equal amounts. No CO was found. All of these products have excellent thermodynamic probabilities for existence.

Krieger and Johnson[1] have suggested two possible mechanisms for oxidation of acetylene in the presence of silver nitrate catalysts: the first involved a critical array or amount of acetylene necessary for oxidation, and the other a promoter action of an intermediate (possibly a silver acetylide). If some critical array is necessary, reaction ought not to occur until some critical amount of acetylene is sorbed. If, on the other hand, silver acetylide promotion is responsible for oxidation, at most a small amount of sorbed acetylene would be required for oxidation by the silver nitrate. Table III summarizes the data used in distinguishing between these possibilities.

The total amount of acetylene that can be taken up without oxidation even at 149° was estimated from the following experiments.

1. When more than 0.166 mole of acetylene per mole of silver nitrate is admitted to the system and then the unsorbed gas is pumped out before 0.166 mole per mole has been sorbed, the gas collected contains only acetylene.

TABLE III

SORPTION OF ACETYLENE BY SILVER NITRATE AT 149° (DETERMINATION OF SORPTION WITHOUT REACTION)

Run no.		NB2-63	NB2-64		NB2-65
			Part I	Part 2	
Pressure, mm.	Initial	10.8	3.5	3.5	4.3
	Final	7.2	0.0	2.0	0.1
Amount gas, mole × 10^5	Initial	15.43	5.22	4.91	6.39
	Final	10.44	0.0	3.19	0.54
Amount $AgNO_3$, mole × 10^5		34.5	35.3	35.3	35.3
Composition residual gas (% C_2H_2)		100	...	..	...
Equilibrium time, min.		...	30.0	92.0	54.0
Contact time, min.		20.0	243.0	112.0	120.0
Molar ratio $\frac{(C_2H_2 \text{ taken up})}{(AgNO_3 \text{ charged})}$		0.145	0.134	..	0.166

2. When less than 0.166 mole per mole of acetylene is admitted, it is all sorbed; and the admission of a second portion of acetylene, large enough to bring the total to more than 0.166 mole per mole, results in further sorption. Excess gas pumped out is then found to contain oxidation products.

3. When just 0.166 mole per mole of acetylene is admitted, it is all sorbed and no gas can be pumped off, even after times much longer than those required to give oxidation products in 2 above.

Partial confirmation of these data is to be found in the observation at lower temperature, where no oxidation took place, that sorption of 80 to 85% of the saturation amount of acetylene marked a point at which a radical lowering of rate of sorption occurred. If the 80% figure is assumed to be approximately correct at 149°, it would correspond to a total uptake of 0.175 mole per mole of acetylene. Since some of the acetylene taken up was oxidized, the latter figure is somewhat high. It thus appears that the critical sorbed concentration of acetylene is not less than 0.166, nor more than 0.175 mole per mole of silver nitrate.

Cook and Oblad[3] have described what may be an analogous situation to that found here. They concluded that catalytic reactions may be preceded by a chemisorption process and that only a very small amount of "catalytic" adsorption may be necessary for reaction. The bulk of the sorbed material would then merely fill up the potential "well" and not participate directly in reaction. The relative amount of "catalytic" adsorption would depend on the depth of the potential "well" for chemisorption, and a high heat of sorption would increase this depth and make the "catalytic" sorption appear to be relatively small. The "catalytic" adsorption would be a kind of chemisorption, but the converse is not necessarily true.

C. Energy of Activation.—In an attempt to approximate the energy of activation, it was assumed that the rate of sorption is proportional to $e^{-E_a/RT}$, in which E_a is the energy of activation. The reliability of the calculation is likely to be enhanced by comparing runs which had almost the 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.)	(Rate)$_1$ × 10^3	(Rate)$_2$ × 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.

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

PHILADELPHIA, PENNSYLVANIA

[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).