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The Reaction of Acetylene–Air Mixtures with Supported Silver Nitrate

BY K. A. KRIEGER

In the course of a study of methods for the removal of traces of acetylene from air, we have investigated the reaction of silver nitrate on various inert supports with air–acetylene mixtures.[1] These studies suggest the existence of a critical lower limit for the concentration of active component. We find that the concentration of silver nitrate required to produce measurable activity is a function of the surface area of the support material and is relatively independent of the structure of the support.

Experimental

Materials.—Silver nitrate was J. T. Baker C. P. grade, used without further purification.

Activated Alumina and Tabular Alumina were obtained from the Alumina Ore Company and used as received.

Prest-O-Lite acetylene was used usually without further treatment, but sometimes purified by passage through sodium bisulfite and sodium hydroxide solutions. No difference in behavior was observed. Measured quantities were introduced into steel pressure cylinders and made up to a total pressure of about 3000 lb./sq. in. with compressed air.

The oil used in the oil saturator was Socony-Vacuum DTE Heavy.

Catalysts were prepared by impregnation of the support with cold aqueous solutions of silver nitrate, followed by slow evaporation of the excess water at its boiling point and final drying at 100°. In all the preparations the weight of support and volume of impregnating solution were kept approximately constant, the concentration of solution being varied to give the desired final silver content. Activation was by heating in air for two hours at 200°, except as noted.

Methods and Apparatus.—As the primary purpose of this program was to find catalysts suitable for the removal of acetylene from air of composition similar to that at the output of oil lubricated compressors designed for air liquefaction equipment, the catalytic apparatus was set up to simulate these conditions. Air–acetylene mixtures were introduced into the apparatus through a reducing valve and rotameter, then passed through water saturator, oil saturator and reaction chamber, each electrically heated. The reaction chamber was a short length of stainless steel pipe provided with a thermocouple well. The water saturator was maintained at 65° and the oil saturator and catalyst chamber at 149°. Temperature could be controlled to about ±2°. In all runs the space velocity was 100,000 (S.T.P.) per hour, and the pressure 100 lb./sq. in. gage. Twenty cc. of catalyst was used in each run.

Known volumes of gas were collected for analysis through by-passes located immediately before and after the catalyst chamber, and acetylene was determined by a modification of the Ilosvay procedure.[2]

The operation of the apparatus has been described elsewhere.[1]

The catalytic activities reported are the results of at least two determinations and the reproducibility is of the order of ±3%.

Surface areas were measured with nitrogen using the BET method[3] and apparatus described by Krieger.[4]

X-Ray data were obtained with a Norelco X-ray Spectrometer using Cu Kα radiation.

Results and Discussion

The data obtained with Activated Alumina F-10 as support are shown in Table I. In this table the surface area has been calculated on two bases, S_c being the area per gram of catalyst and S_s the area per gram of support. S_{cx} is the area of the "exhausted" catalyst per gram of catalyst. The catalytic activity is expressed as per cent. acetylene removed from the air–acetylene mixture, A_3 being the activity after three hours operation and A_0 the activity at the beginning of the run. Under X are recorded the relative concentrations of silver nitrate and under Y those of metallic silver, as

TABLE I

CATALYSTS CONTAINING SILVER NITRATE IN VARYING CONCENTRATION ON ACTIVATED ALUMINA F-10

Cat.	Silver content %	Area, sq. m./g. S_c	S_s	S_{cx}	A_3, %	A_0, %	X_t (Arbitrary units)	X_x	Y_x
	1. Catalysts Tested with 4–6 p. p. m. Acetylene								
F-10	0	128	128		0	0	0	0	0
226	1.10	125	127	62	0	0	0	0	0
227	2.08	132	136	..	0	0	0	0	0
232	3.08	130	137	94	0	30	0	0	0
...	4.06	122	130	..	..	...	0	..	..
228	4.89	114	124	..	0	100	0	0	0
233	5.22	110	120	91	9	92	0	0	0
...	6.19	108	120	..	..	...	0	..	..
230	7.55	106	120	..	69	100	5	0	6.5
217	7.84	100	114	91	81	100	6	0	6
...	9.02	96	112	..	..	...	11	..	..
234	9.54	100	118	82	71	100	14.5	0	7
192	9.67	97	114	86	88	100	11.5	0	6.5
236	11.20	92	112	..	88	100	13.5	0	11
221	13.60	75	95	83	92	100	16	0	8
...	14.55	73	95	..	..	...	18	..	..
239	17.75	57	79	..	92	100	23.5	0	8
222	19.08	46	66	..	93	100	21	7.5	6.5
229	20.28	49	72	71	95	100	19.5	12	6.5
...	21.94	37	57	..	..	...	23	..	..
235	22.44	35	54	..	82[a]	100	18.5	..	..
216	24.52	32	52	67	94	100	25.5	14.5	6
223	28.46	18	33	37	97	100	21.5	17	5
	2. Catalysts Tested with 8–10 p. p. m. Acetylene								
206	1.02	132	134	98	0	0	0	0	0
205	2.01	133	137	97	0	0	0	0	0
204	4.96	120	130	88	0	88	0	0	0
211	6.98	101	113	84	8	100	0	0	6.5
225	7.89	97	111	85	54	100	10.5	0	0
192	9.67	97	114	..	67	100	11.5	0	6.5
221	13.60	75	95	..	68	100	16	0	8.5
222	19.08	46	66	74	75	100	21	7.5	5
212	19.72	44	64	71	84	100	22	9	6.5
224	24.16	29	47	..	75	100	19.5	13	5
223	28.46	18	33	..	82	100	21.5	14	3

[a] Probably heated above 200° during activation.

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(1) Annual Reports of the Thermodynamics Research Laboratory, University of Pennsylvania. Navy Contracts NObs-2477, July 1, 1945, to April 30, 1946; *ibid.*, May 1, 1946, to June 30, 1947; *ibid.*, July 1, 1947, to June 30, 1948.

(2) Geissman, Kaufman and Dollman, *Ind. Eng. Chem., Anal. Ed.*, **19**, 919 (1947).

(3) Brunauer, Emmett and Teller, THIS JOURNAL, **60**, 309 (1938).

(4) Krieger, *Ind. Eng. Chem., Anal. Ed.*, **16**, 398 (1944).

determined by the intensity of X-ray diffraction, the subscripts f and x referring, respectively, to fresh catalysts and those partially exhausted by four hours of use.

The rapid decline in catalytic activity with use as shown by the differences between A_0 and A_3 raises the question as to whether the reaction is actually catalytic. Although under these conditions the total acetylene removed has never exceeded the ratio of one mole of acetylene to one of silver nitrate, other experiments[5] with higher acetylene and lower oxygen pressures have given a ratio greater than one. Since catalytic action is normally preceded by the formation of a complex between reactant and substrate, our conclusions would not, moreover, be affected even if the reaction were not truly catalytic.

Silver Concentration and Activity.—The very sudden rise in A_3 beginning at about 5% and approaching a maximum at about 12% is a striking feature of these data (Fig. 1), and as it can be calculated from the dimensions of the silver nitrate unit cell that about 12% silver would be required to produce a monolayer of the salt, it is tempting to ascribe the maximum to the completion of such a layer. Such a layer would not, however, be expected to yield a sharp diffraction pattern and Figure 2 shows that a strong pattern is produced considerably before 12% silver concentration is attained. As all of the diffraction patterns exhibited sharp lines we are compelled to conclude that even at the lowest concentrations which yield diffraction lines the silver nitrate crystals contain at least several hundred silver atoms, and that the failure to detect them at lower concentrations is to be attributed to limitations imposed by the sensitivity of the method itself. A comparison of A_0 with A_3 will show, furthermore, that the correspondence of X-ray detectable silver nitrate with catalytic activity does not hold where the activity is measured at the beginning of the run. The behavior of a second series of catalysts in which Tabula Alumina T-72 was used as support provides additional evidence against the monolayer hypothesis. Since the area of this support is about 0.2 sq. m./g. compared with nearly 130 sq. m./g. for F-10, maximum catalytic activity, if conditioned exclusively by the completion of a monolayer, should appear at about 1/600 of the silver concentration required to produce it on the high area support. The data of Table II demonstrate, however, that on T-72 maximum activity is not reached until the silver concentration is at least one-fifth of that required on F-10. This latter observation strongly suggests that in the case of the high area porous support a very considerable fraction of the silver nitrate is contained in pores so small that it

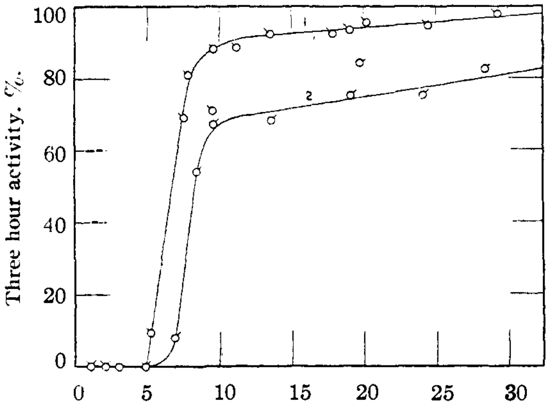

Fig. 1.—Catalytic activity *vs.* silver concentration on activated alumina F-10: ò 1, with 4–6 p. p. m. of acetylene; ó, 2–10 p. p. m. of acetylene,

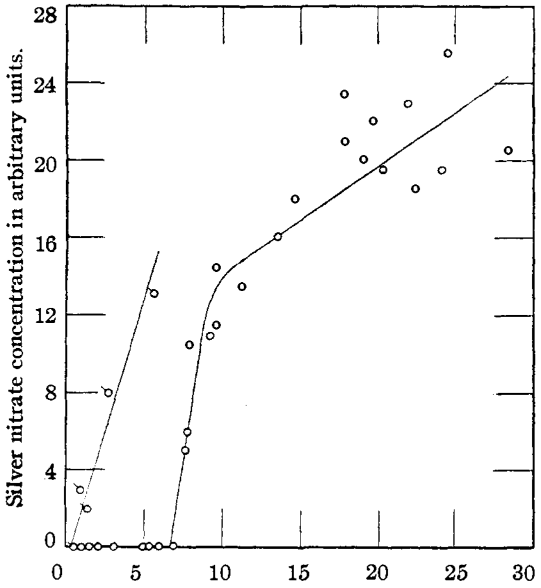

Fig. 2.—Crystalline silver nitrate content as a function of total silver concentration: ○ on F-10; ò on T-72.

TABLE II

CATALYSTS CONTAINING VARYING CONCENTRATIONS OF SILVER NITRATE ON TABULAR ALUMINA T-72; 5 P. P. M. ACETYLENE

Cat.	Silver content, %	A_3, %	A_0, %	X^f (arbitrary units)
T-72	0	0	0	0
256	0.56	0	39	0
253	0.74	0	39	3
257	1.37	21	69	2
252	2.09	18	75	..
254	2.71	33	70	8
255	3.34	33	70	..
251	4.57	44	74	..
258	5.48	44	72	13
250	7.14	52	76	..
259	8.22	44	77	..
260	13.24	53	78	..

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(5) To be published.

is catalytically inactive because diffusion limits access of the reactants to, or removal of the products from, the active surface. Taken in conjunction with these facts the similar maximum activities of catalysts prepared upon supports of such widely different areas points to catalytic activity confined to the "external" surface of the granules and practically precludes the possibility of specific effects due to differences in the support materials.

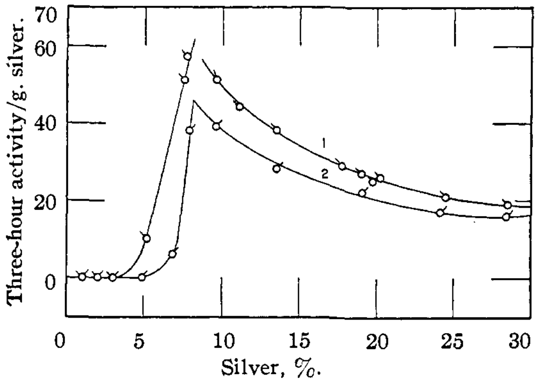

Fig. 3.—Catalytic activity per gram of silver *vs.* silver concentration: 1, with 4–6 p. p. m. of acetylene on activated alumina F-10; 2, with 8–10 p. p. m. of acetylene on activated alumina F-10.

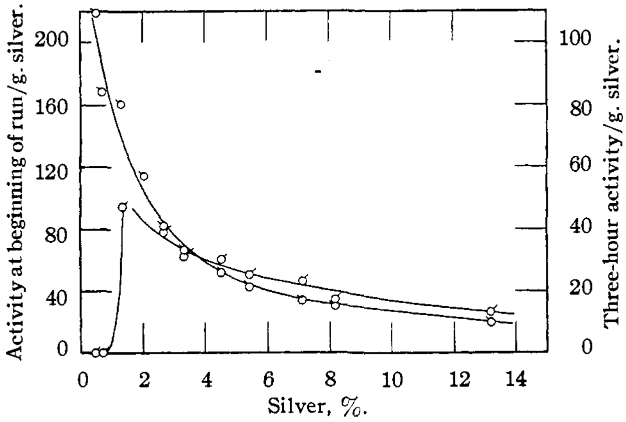

Fig. 4.—Catalytic activity as a function of silver concentration on T-72; 5 p. p. m. of acetylene: ○, A_0; ○, A_3.

The fact that the ratio of silver concentrations required to give measurable X-ray diffraction intensities on the two supports (Fig. 2) is of the same order as that needed to produce maximum values of A_3 seems to support the belief that the carriers are almost entirely non-specific in their action, functioning merely to provide more or less extended areas upon which the silver nitrate may be spread.

Although the close correspondence between the silver concentration required to give detectable diffraction effects and that at which A_3 is greater than zero must be regarded as fortuitous, the fact that the break in the curve for F-10 supported catalysts (Fig. 2) corresponds in silver concentration to the leveling off in Fig. 1 may be interpreted to mean that the thickness of the silver nitrate layer has become sufficiently great so that the lower layers contribute little either to catalytic activity or to diffraction intensity.

All of these data require that an explanation other than the completion of a monolayer be found for the sudden increase in activity with rising concentration. The nature of the problem can perhaps be clarified by plotting the specific activity (per gram of silver) as a function of silver concentration. This has been done in Figs. 3 and 4, inspection of which will show that there are two distinct regions to be accounted for. The higher concentration range, where the specific activity decreases with increasing concentration, is the more easily understood. Recent work[6] has shown that the specific activity of copper oxide and of chromia on alumina steadily decreased with increasing concentration of the active component and that at least in the case of chromia there was a distinct correlation between activity and dispersion as indicated by measurements of magnetic susceptibility. Selwood very reasonably interprets these results to mean that a high degree of dispersion is favorable to good catalytic activity. Though our data at higher concentrations support these experimental findings, the probability of occlusion of part of the silver nitrate in pores of the support or by overlying additional layers of the salt appears to offer an alternative explanation for the decrease in specific activity at the higher concentrations. The latter explanation may be offered with greater confidence in the case of catalysts supported on T-72, since even at the lowest concentrations studied there is enough silver nitrate present to furnish a covering ten "molecules" thick, and it is difficult to understand how the effective dispersion could change much in the higher concentration range.

The abrupt rise in activity (A_3) at lower concentrations is remarkable in that it does not begin at the concentration origin but is delayed to about 5 and 1% silver on F-10 and T-72, respectively. This observation would not be surprising if the supports themselves possessed any catalytic activity, since examples of this sort of promoter action are well known. Separate experiments have shown, however, that neither support has measurable activity by itself, and we have been unable to discover similar phenomena in the literature. It is worth noting that Selwood, whose measurements dealt in part with the same variables considered here, though in very different chemical systems, did not find a maximum.

There are several possible explanations for the delayed appearance of catalytic activity. The assumption might be made that a certain minimum "crystal" size of active component is necessary for activity. Such an assumption is not in itself un-

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(6) Selwood and Dallas, THIS JOURNAL, **70**, 2145 (1948); Eischens and Selwood, *ibid.*, **70**, 2271 (1948); **69**, 2698 (1947).

reasonable, for it is generally recognized that heterogeneous reactions are normally preceded by an activated adsorption resulting from the operation of rather strong forces between catalyst and reactant. As these forces are clearly of the same general kind as those responsible for crystal growth, and are therefore probably coöperative in nature, it might be expected that they will not reach important magnitudes until the crystals attain sizes larger than those which correspond to the collection of but a few molecules. It should be emphasized that this picture does not conflict with Selwood's arguments in favor of a direct relationship between dispersion and activity, but simply serves to set a lower limit to the permissible dispersion. If this assumption is to be entertained, however, it is pertinent to inquire why Selwood did not find a similar maximum, and the explanation is perhaps to be found in the very different properties of the active materials in his experiments. Chromia and copper oxide are obviously substances in which the cohesive forces are very much greater than those in silver nitrate, as is evidenced, for example, by their much higher melting points and greater thermal stabilities, and it is quite possible that these cohesive forces are great enough to entirely prevent dispersion to the extent required to produce a diminution in activity or at least to limit such dispersion to still lower concentration ranges than those reported. It is a corollary of this explanation that maxima such as we have found ought to occur most readily when the active material is of low melting point.

Alternative explanations for the delayed rise in activity are possible, however. Since both oil vapor and acetylene, to a lesser extent, are known to cause a decrease in activity with time, it might be argued that the effects observed are due merely to the inactivation of the surface by these means. But experiments in which the time of exposure to oil vapor was purposely varied produced no appreciable effect and since the acetylene concentration does not much affect the position of maximum specific activity (Fig. 1), it does not appear that the observations can be accounted for exclusively by these processes.

A second explanation requires the assumption that small quantities of silver nitrate are lost by reaction with the support material to yield a compound not catalytically active. Although it is practically impossible to entirely rule out this possibility, since very small amounts of impurity might under certain circumstances have large effects, it is difficult to believe that the loss of as much as 5% silver could be accounted for by this means, and still more difficult to explain the relationships observed on high and low area supports in this way.

On the whole the catalytic evidence strongly suggests that crystal size has an important role in determining activity.

Surface Area and Activity.—The variation of surface area, per gram of support (S_s of Table I) with silver content is shown in Fig. 5, where the solid line is the least squares line calculated from all the points except "A." A decrease in area with rising concentration of active component has been observed before[6] and is what would be expected where a substance of low specific area covers pores in one of much higher area. Because of the scatter of experimental points, it is difficult to be sure that the slight rise in area up to about 3% silver is real, but there can be no question that other straight lines drawn through point "A" would not fit the data nearly so well, and it seems quite safe to say that the area does not begin to decrease significantly below about 5% silver. This observation again suggests that at low concentrations the crystals of silver nitrate are too small to effectively close the pores of the support,

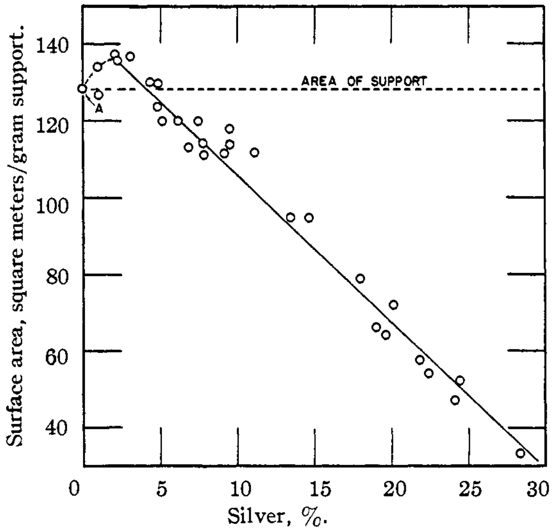

Fig. 5.—Surface area as a function of silver concentration on activated alumina F-10.

The effects of concentration on catalytic activity and surface area are all consistent with a picture of the catalyst as a collection of silver nitrate crystals, held mechanically on the carriers, whose size depends upon the surface concentration of the salt and whose activity in turn depends strongly upon size below a certain minimum size. At silver concentrations below about 12% on F-10 and about 2% on T-72 these crystals are discrete, but at higher concentrations they substantially cover the external surface of the supports.

Activation Temperature and Activity.—The effect of alterations on the time and temperature of activation are shown in Fig. 6. Both relative shapes and relative placement of the curves for one and two hour activation times indicate that the decline in activity occurring beyond the maximum is due to decomposition of the silver nitrate. In this connection the rise in area is significant; since it is found to correspond closely with the decrease in activity it may be interpreted to represent the gain in area resulting from the decomposition of relatively compact silver nitrate crystals. Separate experiments have shown only a very slight decrease in the area of the support itself over the 200–400° temperature change. The sharp rise in activity to the maximum is probably associated with dehydration of the silver nitrate.

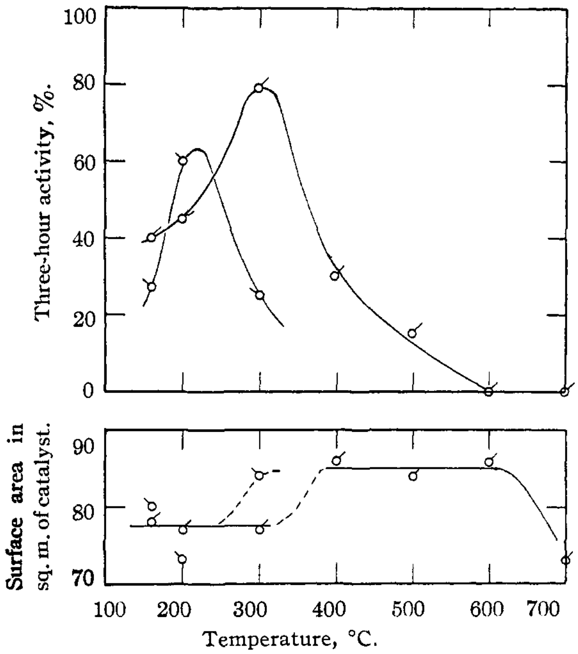

Fig. 6.—Activity and surface area as a function of time and temperature of activation, F-10, 5 p. p. m. C_2H_2: ♂, 1 hr. activation; ɓ, 2 hr. activation.

Exhausted Catalysts.—During operation, changes in surface area and partial conversion of silver nitrate to metallic silver occur. Figure 7 (X_x and Y: of Table I) illustrates the latter change. Comparison of these data with those of Fig. 2 demonstrates that the minimum silver concentration required to yield detectable silver nitrate in fresh catalysts is very nearly the same as that required for metallic silver in an exhausted one and that for concentrations up to about 15% no crystalline silver nitrate is left unconverted by four hours of operation. That the diffraction intensity of silver does not continue to rise with increasing silver content means that conversion of silver nitrate to silver proceeds only to a fixed depth, no doubt because the silver itself protects the lower layers from attack. The slight but measurable decrease in silver intensity, coincident with the first appearance of unreduced silver nitrate at about 15% total silver, is probably due to the solvent effect of silver nitrate. The curve for silver nitrate intensity *vs.* total silver is practically congruent with that found for fresh catalysts (Fig. 2) but is translated to about 10% higher total silver concentrations; the magnitude of this translation sets only an upper limit to the amount of silver nitrate decomposed during operation, because a correction of unknown size would have to be applied to the diffraction intensities observed in exhausted samples on account of the screening effect of the overlying layer of metallic silver. Data for a similar set of catalysts run with 10 p.p.m. of acetylene (Table I) give curves indistinguishable, within the experimental error, from Fig. 7.

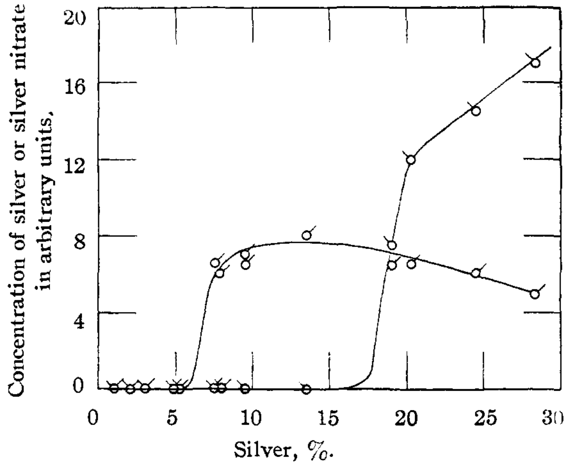

Fig. 7.—Crystalline silver and silver nitrate concentration on exhausted catalysts as a function of total silver concentration on F-10, 5 p. p. m. of C_2H_2: ♂, silver; ɓ, silver nitrate.

Changes in surface area with use are shown in Table I and Fig. 8. The decrease in area at low silver concentrations is to be attributed to covering of exposed support surface by deposited oil vapor. As the silver concentration rises, so that more and more of the support surface is protected from oil vapor by silver nitrate, the decrease in area becomes less, and at about 12% silver the

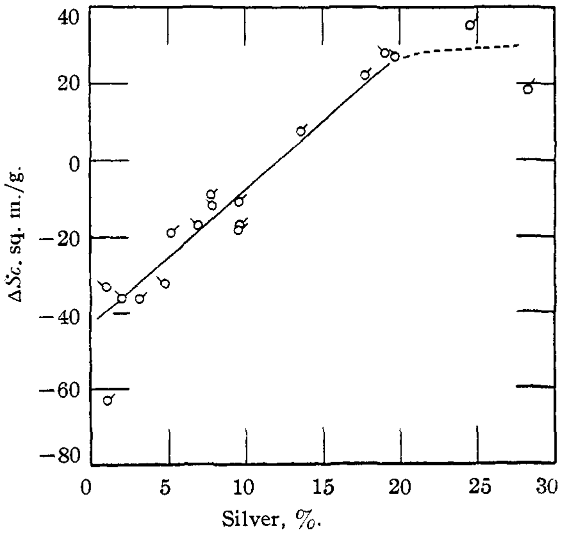

Fig. 8.—Change in surface area during use as a function of total silver content on F-10: ♂, 5 p. p. m. of acetylene; ɓ, 10 p. p. m. of acetylene.

area does not change during use. It is noteworthy that this is about the silver concentration at which the catalytic activity levels off. The increase in area at still higher concentrations is probably due to increases in the area of the upper layers of the silver nitrate itself, accompanying its reduction to metallic silver, which has already been shown to occur. If this latter supposition is correct the increase in area might be expected to become nearly constant at the higher concentrations since data presented earlier indicate that only a limited amount of decomposition can occur. The points lying above 15% total silver which represents the largest amount of silver nitrate which can be decomposed under these conditions, do in fact suggest such a leveling off with ΔS_c equal to about 30 sq. m./g.

Acknowledgment.—The author wishes to express his thanks to the Thermodynamics Research Laboratory of the University of Pennsylvania and its sponsors the Navy Department, Bureau of Ships, for the support of this project, to Dr. T. A. Geissman for the design of the apparatus and for many contributions to the planning of the program, and to Messrs. D. Y. Dolman, R. F. Cree, Philip Mahoney and E. A. Fiero for much of the experimental work.

Summary

1. The activity of silver nitrate supported on alumina for reaction with acetylene–air mixtures has been studied as a function of silver nitrate concentration, area of support, temperature of activation, and acetylene concentration. Surface areas and X-ray diffraction patterns have been determined.

2. The activity is found to depend upon the ratio of surface area of support to concentration of silver nitrate, and arguments are advanced to show that maximum activity is attained when the support is covered with a multi-layer of silver nitrate.

3. Evidence is presented which leads to the hypothesis that a certain minimum crystal size is required for reactivity.

4. The effect of changes in activation temperature is related to chemical changes in the silver nitrate.

5. Factors causing decreased activity during the reaction are analyzed, and reduction of silver nitrate in the active layer is shown to occur to a limited extent. The change in surface area during use is found to be related to the decline in activity.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

New Synthetic Methods for the Preparation of Lysine[1]

BY DAVID CYR SAYLES[2] WITH ED. F. DEGERING

Many syntheses of lysine have been published,[3] but only the von Braun[4] method and its improvement by Eck and Marvel[5] and Galat[6] seem to have commercial application. More recently, two closely related syntheses of DL-lysine, using dihydropyran as starting material[7,8] have been published by Rogers[7] and Gaudry.[8]

During this research, several methods were investigated. The first involves the splitting of ε-caprolactam[9] by hydrochloric acid and neutralization to give 6-aminohexanoic acid.[10] The rest of the process is similar to that developed by Eck and Marvel.[11] The ammonolysis of 2-bromo-6-benzoylaminohexanoic acid, however, is effected by the use of aqueous ammonia and ammonium carbonate in the presence of cuprous chloride, with a decided increase in yield.

Several methods which entail the use of 1-bromo-4-chlorobutane and 1-chloro-4-nitrobutane were investigated. These intermediates are prepared by direct chlorination of 1-bromobutane and 1-nitrobutane, respectively, in yields of 30–40%. Their utilization in the preparation of lysine are indicated by: n-BuBr → $Cl(CH_2)_4Br$ (35%) → $Cl(CH_2)_4CH(CO_2Et)_2$ (65%) → $Cl(CH_2)_4CBr(CO_2Et)_2$ (70%) → $Cl(CH_2)_4CHBrCO_2H$ (50%) → lysine dihydrochloride (55%).

n-$BuNO_2$ → $Cl(CH_2)_4NO_2$ (35%) → $O_2N(CH_2)_4CH(CO_2Et)_2$ (20%) → $O_2N(CH_2)_4C(:NOH)CO_2Et$ (25%) → $H_2N(CH_2)_4CHNH_2CO_2Et$ (9%) → lysine dihydrochloride (5%).

1,4-Dichlorobutane was first converted to 1-chloro-4-phenoxybutane, as indicated by: $Cl(CH_2)_4Cl$ → $PhO(CH_2)_4Cl$ (60%) → $PhO(CH_2)_4CHAcCO_2Et$ (40%) → $PhO(CH_2)_5CO_2H$ (50%) → $PhO(CH_2)_4CHBrCO_2H$ (85%) → $Br(CH_2)_4CHBrCO_2H$ (87%) → lysine dihydrochloride (81%).

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[1] This paper was reported at the Washington meeting of the American Chemical Society in September, 1948.

[2] Present address: Lowe Brothers Company, Dayton, Ohio.

[3] C. L. A. Schmidt, Editor, "The Chemistry of the Amino Acids and Proteins," 2nd ed., Charles C. Thomas, Baltimore, Md., 1944.

[4] J. von Braun, *Ber.*, **42**, 839 (1909).

[5] J. C. Eck and C. S. Marvel, "Org. Syntheses," **19**, 18, 20, 61 (1939).

[6] Galat, THIS JOURNAL, **69**, 86 (1947).

[7] Rogers, Emmick, Tyran, Levine and Scott, report given before the Organic Division of the American Chemical Society at St. Louis in September, 1948.

[8] Gaudry, *Can. J. Research*, **26B**, 387 (1948).

[9] Available from E. I. du Pont de Nemours & Company, Wilmington, Delaware.

[10] Eck, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., 1943, p. 28.

[11] Eck and Marvel, *J. Biol. Chem.*, **106**, 387 (1934).