investigated.   Near the low limit of this pressure however the atoms and radicals have a 1000:1 chance to diffuse to the walls before reaction.   Thus it becomes necessary to assume that the ratio $\kappa_2^2/\kappa_1\kappa_5$ is the same for wall and gas reactions.

While this new assumption is not very satisfactory, it offers at any rate new means of testing the theory by studying ammonia decomposition at low pressures in vessels with walls prepared either to accelerate or retard the hydrogen atom recombination.   Such experiments are considered for the near future by one of us.

Concluding, we would like to thank Professor G. S. Forbes for his frequent help and the loan of some of the equipment used in this work.

Summary

1.   The gaseous products of the photochemical ammonia decomposition are a 1:3 nitrogen–hydrogen mixture even under conditions excluding a photochemical decomposition of hydrazine.

2.   The quantum yield of ammonia decomposition at room temperature is 0.25 independent of pressure, light intensity and time of illumination.

3.   At 500° the quantum yield is 0.5 or more.

4.   The bearing of these results on other work on ammonia decomposition is discussed and a mechanism of ammonia decomposition is developed.

CAMBRIDGE, MASSACHUSETTS

THE SORPTION OF GASES BY IRON

BY ARTHUR F. BENTON AND T. A. WHITE[1]

Introduction

As a result of numerous researches in recent years in the field of adsorption of gases by catalytically active solids, three processes, apart from compound formation, have become clearly recognized—physical adsorption, activated adsorption and solution.   The characteristics and interrelationships of the two types of *ad*sorption are now reasonably clear.[2]

In the attempt to distinguish adsorption from solution, it has been customary to assume that the former is always rapid, while the latter is ordinarily slow.   However, since it has been shown that activated ad-

[1] Du Pont Fellow in Chemistry.

[2] (a) Benton, THIS JOURNAL, 45, 887, 900 (1923);   (b) Benton and White, *ibid.*, 52, 2325 (1930);   (c) Taylor, *ibid.*, 53, 578 (1931);   (d) Taylor and Williamson, *ibid.*, 53, 2168 (1931);   (e) Taylor and McKinney, *ibid.*, 53, 3604 (1931);   (f) Benton and White, *ibid.*, 54, 1373 (1932).

sorption may be a slow process,[2b-f,3] it is clear that rate alone is not a certain criterion.   Nevertheless, in the systems copper–hydrogen and copper–carbon monoxide, it was shown[2f] that by suitable procedures involving both equilibria and rates, activated adsorption and solution could be sharply differentiated, and the contributions of each to the total sorption under any conditions could be separately estimated.   In the work here reported, the same methods have been applied in a study of the sorption of nitrogen, hydrogen and carbon monoxide by reduced iron.

No extensive investigations of sorption by iron have previously been reported.   Sieverts[4] found the solubility of hydrogen in iron wire at 400° was very small, but increased with rising temperature; nitrogen dissolved in gamma but not in alpha iron.   The "adsorptions" at lower temperatures have been examined by Taylor and Burns[5] and by Nikitin.[6]

Experimental Details

Since many of the experiments were continued over long periods, it was considered desirable to insure against leaks by substituting mercury seals for stopcocks.   The apparatus has already been described.[2b]   The sorption under any given conditions of pressure, temperature and time was determined as the difference between the volume of gas admitted to the bulb containing the iron, and the volume remaining in the free space. The latter was obtained by experiments with helium in the manner previously described.

The sorbent (Iron I, 54.6 g.) was prepared from an 8–14 mesh sample of fused ferro-ferric oxide, containing 0.15% of alumina, for which we are indebted to Dr. P. H. Emmett of the Fixed Nitrogen Research Laboratory, Washington.   The oxide was reduced *in situ* in a current of hydrogen for five days at 375° and for fourteen days at 425–450°. Evacuation between runs was carried out at 500° by means of a Töpler pump.

Occasional check runs made at intervals throughout the work revealed no trend in the activity or capacity of the sample.   Hence the data obtained for different gases, and for the same gas under different conditions, are directly comparable.

All volumes are given in cc. at 0°, 760 mm., and all pressures in mm. of mercury at 0°.

Results with Nitrogen

The isothermal adsorption of nitrogen at temperatures from -191.5 to 0° is shown in Fig. 1, Curves 1, 2, 3, 4.   In this and later figures open circles indicate points obtained from lower pressures, that is, after a fresh addition of gas to the bulb; black circles (and other solid figures) are used for points obtained by the reverse process.

The rate of adsorption at -183, -78.5 and 0° was apparently instantaneous.   At $-191.5°$ equilibrium was attained in a few minutes.   The fact that the equilibrium was actually reached is shown by the close agreement of points obtained from higher and from lower pressures.

[3] Benton and Elgin, THIS JOURNAL, **48**, 3027 (1926); **49**, 2426 (1927).

[4] Sieverts, Z. physik. Chem., **60**, 129 (1907).

[5] Taylor and Burns, THIS JOURNAL, **43**, 1273 (1921).

[6] Nikitin, J. Russ. Phys.-Chem. Soc., **58**, 1081 (1926); Z. anorg. allgem. Chem., **154**, 130 (1926).

The observed effects of temperature and pressure, together with the practically instantaneous rates, leave no doubt that the sole process occurring here is a surface adsorption of the physical type. Thus, the isotherms show no tendency to reach a saturation limit, and at the higher temperatures the adsorption is very nearly proportional to the pressure.
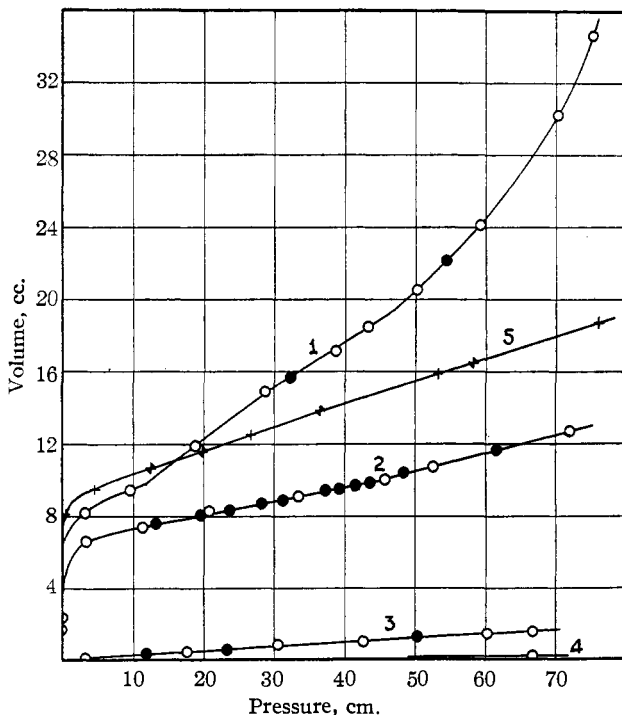

Fig. 1.—Isotherms for nitrogen and carbon monoxide: Curves 1, 2, 3 and 4 are for nitrogen at −191.5, −183, −78.5, and 0°, respectively. Curve 5 is for carbon monoxide at −183°.

Further, at a given pressure the values decrease uniformly with increasing temperature, and the heat of adsorption is relatively small, as shown by the values of Q, in cal. per mole, given in Table I.

TABLE I

HEAT OF PHYSICAL ADSORPTION OF NITROGEN BY IRON I

Vol. adsorbed	p at −191.5°	p at −183°	Q
8.0	22	190	3700
10.0	117	457	2340
12.0	195	641	2050

These heats cover the same range previously found for nitrogen on copper,[2f] and exceed the latent heat of vaporization of nitrogen (1380 cal.) by a factor of only 1.5 to 3.

Higher Temperatures.—The data obtained for the sorption of nitrogen at higher temperatures are given in Table II. These results were obtained by introducing a definite amount (5.91 cc.) of gas into the system, and successively determining the apparent equilibria at the temperatures shown.

TABLE II

SORPTION OF NITROGEN AT HIGHER TEMPERATURES

Temp., °C.	Pressure, mm.	Sorption, cc.
321	418.0	0.43
0	195.1	.42
344	425.1	.54
360	435.6	.56
408	469.6	.54
0	195.1	.42

The sorption at these higher temperatures is considerably greater than at 0°. Since here the physical adsorption must be negligibly small, it is evident that these values represent a second type of sorption. The rate of this process at 0° is very slow, so that little, if any, of the gas taken up at high temperatures is evolved on cooling to 0°.

The data obtained are incapable of furnishing a definite decision as to the nature of the high-temperature sorption. On the other hand, since Sieverts' experiments[4] indicate that gaseous nitrogen at ordinary pressures is insoluble in alpha iron, the evidence points to activated adsorption as responsible for the observed phenomena. This view is rendered still more probable by the fact that at the higher temperatures, iron similar to that here employed is known to activate nitrogen for ammonia synthesis,[7] and there is now available a large body of evidence to support the hypothesis that activated adsorption is an essential step in contact catalysis.

Results with Carbon Monoxide.—The isotherm for carbon monoxide at −183° is plotted in Fig. 1, Curve 5. Here as with nitrogen the rate was instantaneous. Throughout the whole range of pressure the ratio of the adsorption of carbon monoxide to that of nitrogen at this temperature is 1.44 ± 0.02. These facts are convincing evidence that in this case also the process is solely one of physical adsorption.

Measurements were also made with carbon monoxide at −78.5 and 0°, but in neither case was equilibrium reached, even after one hundred hours. Nevertheless, the observed rates clearly show the existence of two different processes. A few typical data on rates are given in Table III; the values shown for zero time are the volumes taken up at the last previous point.

At −78.5° a large fraction of the sorption occurred within three minutes (0.05 hour), after which the rate decreased sharply. At 0° relatively little sorption took place during the first three minutes, but after this time

---

[7] Almquist and Crittenden, *Ind. Eng. Chem.*, **18**, 1307 (1926).

TABLE III

RATE OF SORPTION OF CARBON MONOXIDE

| | −78.5° | | | 0° | |
Time, hrs.	P, mm.	V, cc.	Time, hrs.	P, mm.	V, cc.
0.0	0.0	0.95	0.0	2.0	1.66
.05	59.0	2.84	.05	191.4	2.40
12.1	29.0	4.00	.30	162.1	3.22
15.5	27.3	4.07	1.01	138.7	3.88
19.8	25.5	4.13	3.50	113.4	4.59
21.5	25.0	4.15	5.00	106.0	4.80
			13.0	88.0	5.30
0.05	562.2	5.83	35.6	70.0	5.82
.80	555.2	6.10	74.8	57.7	6.16
14.7	530.3	7.07			
27.4	521.8	7.40	0.05	503.7	6.48
38.6	515.9	7.63	1.22	490.7	6.84
50.7	511.4	7.80	5.9	469.8	7.43
62.9	508.9	7.90	21.8	438.0	8.32
87.2	503.4	8.11	50.2	413.2	9.02

the rate was more rapid than at the lower temperature, and the total sorptions reached after a given time were greater.

These results are precisely what would be expected if the total sorption at these temperatures is a combination of physical adsorption and a second process. Since other surfaces give *physical* adsorptions of carbon monoxide and nitrogen in this range of temperature, which are in the ratio[2f] of about 1.5, it may be calculated that here the adsorption of this type, at 500 mm. pressure, should amount to about 2 cc. at −78.5°, and about 0.2 cc. at 0°. Thus the first, rapid part of the observed sorption, which is much greater at −78.5° than at 0°, can be largely accounted for as physical adsorption. The nature of the subsequent process, whether activated adsorption, carbonyl formation or solution, or a combination of these, has not been ascertained.

Results with Hydrogen

Low Temperatures.—The adsorptions of hydrogen at −195 and −183° are plotted in Fig. 2, Curves 1 and 2. The striking discontinuities in these curves have previously been considered in detail, in connection with a general discussion of stepwise adsorption.[8] Neglecting the discontinuities, one observes that the general shape of the isotherms is typical of physical adsorption. There is little or no adsorption at "zero" pressure, and the values continue to increase with increasing pressure without approaching a saturation limit. At both temperatures the rate was apparently instantaneous, and values obtained from the side of higher pressure are in excellent agreement with those approached from lower pressures. The adsorptions decrease with rising temperature, and the heat of adsorp-

[8] Benton and White, THIS JOURNAL, **53**, 3301 (1931).

tion calculated from the isotherms by the Clapeyron equation is about 1600 cal. per mole.   These observations show that physical adsorption is the sole process occurring.

Curve 3, Fig. 2, represents an isotherm at −78.5°.   These results must be considered in the light of the following observations,   The first two portions of gas admitted to the iron apparently came to equilibrium immediately at pressures of 50 and 258 mm., respectively, but the adsorption in each case was less than 0.05 cc.   The next portion gave an immediate adsorption of 0.30 cc. at 715 mm.   In each of these cases the pressure remained constant for the twenty to thirty minutes of observation.   Part
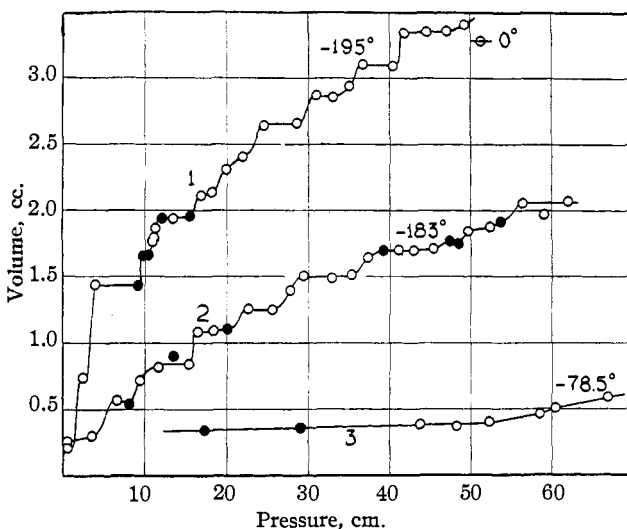

Fig. 2.—Isotherms for hydrogen.

of the gas was then withdrawn from the bulb, with the result that the adsorption at once decreased to 0.05 cc. at 405 mm,   However, this volume did not remain constant, but gradually increased until an apparently constant adsorption of 0.28 cc. was reached after sixteen hours.   From this point on, the values shown in Curve 3 were successively obtained.   At each of these points equilibrium was established very rapidly; even with times of observation as long as twenty-two hours no change in adsorption occurred.   A repetition of this experiment gave practically identical results, except that here the slow adsorption (0.24 cc. at 86 mm.) took place at the first point, where the system was kept under observation for thirty-nine hours.

The behavior noted is readily accounted for as follows.   At −78.5° there is a small, rapid and readily reversible physical adsorption, which exhibits steps similar to those at lower temperatures, but here the first step

occurs at a pressure of about 600 mm. At one point in the course of following this isotherm, where sufficient time was allowed, a very slow activated adsorption of the order of 0.3 cc. occurred. The isotherm subsequently obtained represents the physical adsorption *plus* the 0.3 cc. adsorbed in the activated form. It is remarkable, however, that the activated adsorption, which reached 0.3 cc. in sixteen hours, showed no further increase in three days.

Higher Temperatures.—At 0° there was an immediate adsorption of 0.2–0.3 cc., followed by an extremely slow process which did not come to equilibrium in 35 days. The value reached at the end of this time, 3.28 cc. at 513 mm., is indicated in Fig. 2. At this point the temperature was quickly raised to 110°. The result was a rapid *decrease* of the sorption to 2.06 cc. at 768 mm., but this decrease was followed by a gradual *increase* over a period of three days to 2.47 cc. at 748 mm., without any sign of an approach to final equilibrium.

It may be concluded from these observations that in the neighborhood of 110° the sorption consists of two distinct processes, one of which is rapid and decreases in extent with increasing temperature, while the second is very slow. This conclusion is confirmed by isothermal measurements conducted wholly at 110°, which showed a rapid initial sorption followed

TABLE IV

RATE OF SORPTION OF HYDROGEN AT 110 AND 210°

Time, hrs.	110° P, mm.	V, cc.	Time, hrs.	210° P, mm.	V, cc.
0.0	...	0.0	0.0	...	0.0
.05	22.5	.23	.05	56.5	.38
.12	16.0	.35	.60	48.5	.51
.30	5.0	.58	2.7	45.0	.57
1.72	3.0	.62	6.1	43.0	.60
			25.0	40.5	.64
0.05	113.0	0.69			
.30	102.0	.92	0.05	539.3	1.02
.88	99.0	.98	2.0	522.1	1.30
1.63	97.0	1.02	5.0	516.1	1.40
4.38	93.9	1.08	21.0	505.9	1.57
8.13	92.0	1.12	30.5	503.0	1.62
21.7	88.0	1.20	45	500.5	1.66
			54	499.6	1.67
0.1	315.0	1.42	69	496.8	1.72
1.0	310.0	1.53	78	496.1	1.73
3.0	307.1	1.59	96	493.7	1.77
7.3	303.4	1.66	117	492.4	1.79
24.7	297.7	1.78			
0.05	607.7	1.91			
1.05	605.2	1.96			
4.6	602.2	2.02			
24.3	596.4	2.14			

by a very slow process. At 210° also there was a rapid process, which involved smaller quantities of gas than at 110°, and again a slow process ensued. The sorption at these temperatures as a function of time is given in Table IV.

At the conclusion of the measurements at 110°, when a sorption of 2.14 cc. had been reached, the system was rapidly cooled to −78.5°. At this temperature the sorption became constant almost immediately at 2.38 cc. under a pressure of 305.6 mm. It is evident that the gas taken up at 110° was not desorbed on cooling; on the contrary, an increase of about 0.2 cc. occurred, which is undoubtedly physical adsorption and is of the same order as the physical adsorption on the bare surface at −78.5°.
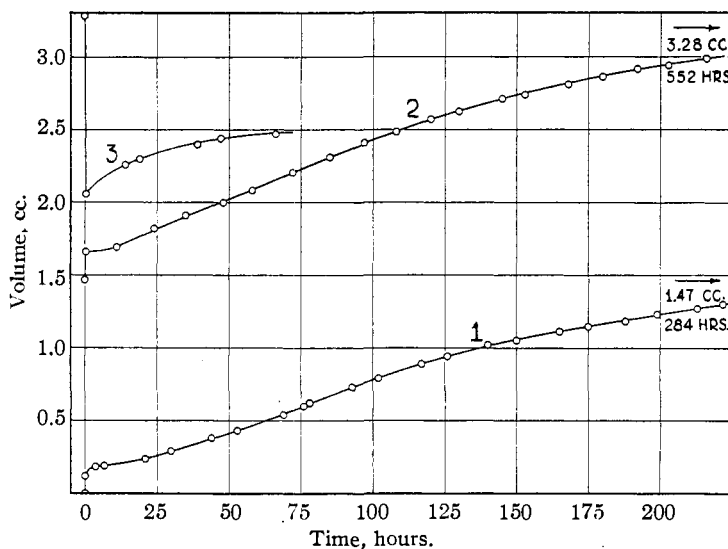

Fig. 3.—Rate of sorption of hydrogen at 0°: Curve 3, after heating
to 110°.

The sorption at 0° as a function of time is shown in Fig. 3, Curves 1 and 2. The range of pressure involved here was as follows: for Curve 1, 120.5 to 72.7 mm; for Curve 2, 570.5 to 512.8 mm. In each case, after a rapid initial adsorption of about 0.2 cc., the rate sharply decreased almost to zero, then gradually increased, and finally fell off again. The change of sorption with time after heating to 110° is shown in Curve 3, which brings out clearly the rapid initial decrease of the sorption, followed by a slow increase.

In interpreting these results it is to be noted that the *physical* adsorption, which had already become very small at −78.5°, must be entirely negligible at 0° and above. The two processes which have been distinguished at 110° may provisionally be regarded as activated adsorption and solution.

On this basis the activated adsorption is very slow at 0°, except for the first 0.2–0.3 cc., but rapidly increases in rate with increasing temperature. The final equilibrium, on the other hand, corresponds to a decreasing activated adsorption with increasing temperature. If on a plot of the volumes taken up at 110 and 210° against the time, the slow process at these temperatures is extrapolated back to zero time, a rough estimate may be obtained of the fractions of the total sorption which are due to each individual process. In this manner it was found that (at 500 to 600 mm.) the activated adsorption amounted to about 1.4 cc. at 110° and 1.0 cc. at 210°; the slow process which has been ascribed to solution amounted to about 0.7 cc. at each temperature, but the time of observation was much longer at 210°, so that equilibrium was doubtless more closely approached. Because of the considerable uncertainty in these values, and because the slow process had certainly not reached equilibrium, the isobars for the different types of sorption will not be given here.

If the above view of the situation is correct, it must be concluded that the process of activated adsorption is *autocatalytic*. Thus at 0°, after about 0.2 cc. had been rapidly adsorbed, an induction period of eight to ten hours occurred, during which there was little further sorption. Subsequently the rate increased, passed through a maximum, and then decreased. This behavior is especially clearly shown by Curve 1 of Fig. 3. At 110°, in spite of the rapid rate of this process, there was some slight evidence of the same phenomenon. It is conceivable that only the few tenths of a cc. which was rapidly taken up at 0° (and slowly at −78.5°) represents activated adsorption, perhaps on the edges of the crystals, and that the autocatalytic process involves the formation of a new solid *phase* of iron hydride. Further data will be necessary before this possibility can be profitably discussed in detail. It may be noted, however, that on this view the rapid decrease in sorption on heating from 0 to 110° would indicate that the hydride is unstable at the latter temperature, even at a pressure of 770 mm.; consequently the rapid process at lower pressures observed in the experiments at 110 and 210° could not be ascribed to the formation of this definite hydride.

Discussion

The results for iron are similar in the main to those previously reported for nickel and copper. At low temperatures all three metals exhibit an apparently instantaneous physical adsorption, which decreases rapidly and uniformly with increasing temperature, corresponding to heats of adsorption which are only about two to four times the latent heat of vaporization of the several gases.

At some point activated adsorption first makes its appearance, and rapidly increases in rate at higher temperatures. On both copper and

iron the rate of this process is considerably greater for carbon monoxide than for hydrogen, and enormously greater than for nitrogen.   Comparison of the different metals shows that the rates of activated adsorption of hydrogen were about equal for the particular samples of nickel and copper employed, but were much less in the case of iron.   The rate with carbon monoxide was much less for iron than for copper.   (The system nickel–carbon monoxide has not been studied from this point of view.)   Doubtless the smaller rates with iron are due in part to the fact that the sample of iron was prepared from fused oxide by reduction at a high temperature, while the other two metals were obtained by cautious ignition of their nitrates and reduction at much lower temperatures.

In many of the cases studied, a third process, provisionally ascribed to solution, has been definitely distinguished.   Such a process occurs in the system, iron–hydrogen.   With nitrogen and carbon monoxide in contact with iron, this third process is not apparent, but it must be noted that in these latter cases the sorptions have been less extensively examined.

Multimolecular Layers at Low Temperatures.—Inspection of Curves 1 and 2 of Fig. 1 reveals the fact that definite "breaks" occur in each case at an adsorption of about 10 cc.   This is apparently the volume of nitrogen necessary to form a complete unimolecular layer of molecules over the surface.   The sharpness of the breaks is no doubt diminished by the incipient formation of a second layer before the first is entirely completed.   At $-191.5°$ there is a second, less definite break at a volume of 19–20 cc., which presumably signifies the completion of the second layer of molecules. From this point on, the adsorption appears to increase in a regular manner, gradually approaching infinity as the pressure increases toward the vapor pressure of liquid nitrogen at this temperature (about 110 cm.).

On this basis the physical adsorptions at the higher temperatures correspond to a very incomplete covering of the surface with a single layer of molecules.   It may be of interest to point out also that the activated adsorption of the various gases never amounts to as much as 10 cc.   From this fact the conclusion may be drawn that activated adsorption does not exceed a unimolecular layer, although the latter is closely approached in the case of carbon monoxide at $0°$.

Summary

The isothermal sorptions of nitrogen, carbon monoxide and hydrogen by reduced iron have been measured at pressures up to one atmosphere and over a range of temperatures down to 78°K.   In many cases also the change in sorption with change in temperature has been examined, with a constant volume of gas in the system.

As in the case of copper previously reported, it is found that in general sorption involves three definitely distinguishable processes, (a) *ad*sorption

of the physical type, (b) *ad*sorption of the activated type and (c) a third process which is probably solution. The contribution of the individual processes to the total observed sorption has been estimated.

The distinguishing characteristics of each process have been further elucidated, particularly in respect to rates, equilibria, heats and thickness of adsorbed layers.

With all three gases at −183° and below, the sorption consists solely of physical adsorption. In each case activated adsorption occurs at higher temperatures. The rate of this process is greatest for carbon monoxide and least for nitrogen. With hydrogen at 110° and above, the third process, ascribed to solution. comes into prominence.

UNIVERSITY, VIRGINIA

THE REACTION BETWEEN OXYGEN AND PROPYLENE: ACTIVATION, OXIDATION AND POLYMERIZATION

BY SAMUEL LENHER

It was recently shown in a study of the reaction between oxygen and ethylene[1] that activation of ethylene was a primary process in the reaction. This activation led to the formation of polymerization and pyrolysis products from ethylene, as well as oxidation products, under conditions where pure ethylene is not decomposed. The formation of the primary oxidation products, ethylene oxide and acetaldehyde containing one oxygen atom and the elements of ethylene in the molecule, and the formation of the polymerization products, propylene, butylenes and amylenes, without separation of hydrogen or direct formation of saturated hydrocarbons or carbon, showed that the activation of ethylene consisted in an activation of the double bond. Since the primary oxidation and decomposition reactions of ethylene could be interpreted adequately by assuming an activation of the double bond under the influence of heat or of oxygen, it seemed of value to determine whether the next member of the mono-olefin series of hydrocarbons, propylene, behaved similarly. The work described in this paper leads to the conclusion that activation of the double bond in propylene is the primary process in the oxidation and polymerization reactions.

The oxidation of propylene has received little attention. In connection with the study of the oxidation of ethylene[2] some experiments on the oxidation of propylene at 280–315° showed that the liquid products of the

[1] Lenher, THIS JOURNAL, 53, 2420, 3737, 3752 (1931).

[2] Lenher, Ref. 1, p. 3748.