range investigated, the transition is so slow that no crystallographic evidence of the monoclinic form could be obtained in these experiments. Welch and Duschak found that the speed of transition was accelerated greatly by water.   In the present experiments water was quite thoroughly removed by continued evacuation at about 325°.

The molar heats of vaporization of the different allotropic forms may be calculated at the temperatures studied with the help of the Clausius-Clapeyron equation.   The calories absorbed in vaporizing 1 g. of the arsenic trioxide are obtained by dividing the molar heat of vaporization by the molecular weight of the vapor (396).   The values are as follows: liquid, 31.5; octahedral, 77.1; monoclinic, (71, estimated).   By subtraction, the heats of fusion and transition may be calculated as follows: octahedral ⟶ liquid, 45.6; monoclinic ⟶ liquid, (39, estimated); octahedral ⟶ monoclinic, (6, estimated).

Summary

1.   The vapor pressures of octahedral and liquid arsenic trioxide have been measured at high temperatures and the equations have been determined.   The vapor pressure of monoclinic arsenic trioxide has been estimated.

2.   The melting point of the octahedral form was found to be 275°, and that of the monoclinic *approximately* 315°.

3.   The heats of vaporization, fusion and transition have been calculated.

4.   The regions of stability of the various allotropic forms of arsenic trioxide have been determined and the influence of the time variable has been discussed.

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THE POLYMERIZATION AND HYDROGENATION OF ETHYLENE BY MEANS OF EXCITED MERCURY ATOMS

BY A. R. OLSON AND C. H. MEYERS

In 1910, Berthelot and Gaudechon[1] demonstrated the chemical effect of ultraviolet light on a number of reactions.   Among the reactions studied were those of the polymerization of ethylene and acetylene.   It is to be remarked that in these experiments, mercury vapor was present in the reaction chamber since the authors state that a solid was quickly deposited on the surface of the mercury.   The importance of this small amount of mercury vapor was emphasized by the work of Cario and Franck[2]

[1] Berthelot and Gaudechon, *Compt. rend.*, **150**, 1169 (1910).

[2] Cario and Franck, *Z. Physik*, **11**, 161 (1922).

in their experiments on the reduction of copper oxide by hydrogen in the presence of excited mercury atoms. The latter authors also showed the necessity of preventing the resonance radiation of mercury, 2536 Å., from being reversed in the arc, and outlined the experimental conditions under which the maximum amount of the mercury resonance line could be made available. During the time that the present authors were studying the hydrogenation of ethylene by the method of Cario and Franck, a number of investigations dealing with various reactions which take place under these experimental conditions have been published. Thus Dickinson[3] has studied the reaction between hydrogen and oxygen; Noyes[4] has studied the reaction between nitrogen and hydrogen and Mitchell[5] has extended Dickinson's work on the reaction between oxygen and hydrogen. Recently a paper has been published by Taylor and Marshall[6] in which they show that hydrogen activated by excited mercury atoms will react with ethylene, oxygen, carbon monoxide and nitrous oxide.

Experimental Procedure

Two series of experiments have been performed. In the first set, light from a 110-volt quartz mercury-vapor arc was concentrated by means of a quartz lens of 5cm. diameter and allowed to fall on the end of a reaction chamber 30 cm. from the lamp. The reaction chamber consisted of a closed quartz tube of 3cm. diameter, one end of which was sealed with a clear quartz plate through which the light entered the chamber. The volume of the reaction chamber was approximately 100 cc. and that of the total line including the reaction chamber and the MacLeod gage to which it was connected was 225 cc. The reaction tube was kept at a temperature of 45° by means of an electric furnace, one end of which was provided with a quartz window. The vapor pressure of mercury was maintained by a small globule of mercury in this tube. Between the reaction tube and the MacLeod gage was inserted a trap, the volume of which was 2% of the total volume so that the effect of lowered temperature on the gas pressure could be observed. To prevent the reversal of the 2536Å. line in the arc, a magnet was used to bend the arc against the wall of the lamp. The lamp was cooled by running water over the cathode and allowing a blast of air to strike the anode.

The hydrogen used in the experiments was generated by the electrolysis of barium hydroxide, passed over heated platinized asbestos and then stored over phosphorus pentoxide. The ethylene was prepared from ethyl alcohol and phosphoric acid, passed through solutions of sodium hydroxide and concd. sulfuric acid, and condensed as a solid

[3] Dickinson, *Proc. Nat. Acad. Sci.*, 10, 409 (1924).

[4] Noyes, THIS JOURNAL, 47, 1003 (1925).

[5] Mitchell, *Proc. Nat. Acad. Sci.*, 11, 458 (1925).

[6] Taylor and Marshall, *J. Phys. Chem.*, 29, 1140 (1925).

in a liquid-air trap.   This ethylene was distilled, and the middle fraction passed into a flask sealed into the line which served as a source of supply.

The gases stored separately were mixed in the reaction vessel.   The amounts were determined by first allowing the hydrogen to flow into the evacuated vessel and reading the pressure on the MacLeod gage and then admitting ethylene and again reading the pressure.   This gas mixture was permitted to stand in the reaction chamber overnight in order to assure uniformity.   The mercury lamp was then lighted, but its rays were not permitted to fall upon the reaction chamber until half an hour had elapsed in order to insure steady conditions.   The course of the reaction was observed by reading the pressure on the MacLeod gage at stated intervals.

The reaction product was determined at least qualitatively by noting the pressure changes in the line when the trap was cooled to —78° (carbon dioxide-ether) and —180° (liquid air).   In those mixtures where hydrogen was the predominant gas, the product was found to be ethane.   In those runs which initially contained only ethylene, we found in addition to ethane a solid deposit which formed on the quartz surface through which the light entered the reaction chamber.   This product was apparent not only by the interference colors produced on the quartz surface but also by its effect in slowing down the rate of subsequent reactions.   The transparency of our cell could be restored by washing it with ether.

TABLE I

REACTION OF ETHYLENE ALONE

Col. A = Time of illumination in minutes.   Col. B = Total pressure in mm. of mercury.

Curve 1				Curve 2					
A	B	A	B	A	B	A	B	A	B
0	0.615	40	0.275	0	0.855	74	0.945	167	0.34
2	.70	45	.24	10	.855	77	.90	177	.34
4	.74	50	.22	20	.855	87	.90	187	.34
6	.74	55	.205	30	.855	97	.90	197	.34
8	.72	60	.19	32	.925	107	.90	212	.28
10	69	70	.175	42	.925	112	.835	227	.24
12	.64	80	.165	52	.925	117	.765	242	.22
15	.59	90	.155	62	.925	122	.70	257	.205
20	.50	105	.15	64	.98	127	.63	272	.195
25	.415	120	.15	66	1.005	132	.575	287	.19
30	.36	180	.15	68	1.01	137	.53	317	.185
35	.305			70	1.00	147	.455	377	.185
				72	0.98	157	.39		

Experimental Results

Reaction of Ethylene Alone.—The data given in Table I are plotted as Curves 1 and 2 in Fig. 1.   These curves are typical of the results we have obtained with pure ethylene.   The flat portions in Curve 2 correspond to times when the arc was intentionally permitted to become heated and show conclusively that there was no appreciable reaction when the 2536 Å. radiation was reversed in the arc.   It is important to notice the increase in pressure at the beginning of a run, obviously due to a decompo-

sition of the ethylene.   In no case does the final pressure approach zero
as would be expected had we pure polymerization.   The final pressure
corresponds very nearly to the increase in pressure near the beginning of
the run and furthermore this increase in pressure was approximately
25% of the initial pressure.   The final pressure showed a small drop when
the trap, mentioned above, was kept at a temperature of —78° for several
hours, corresponding to that expected from the temperature change.
When liquid air was substituted for the mixture of carbon dioxide and
ether, a much greater drop in pressure was obtained than could be ac-
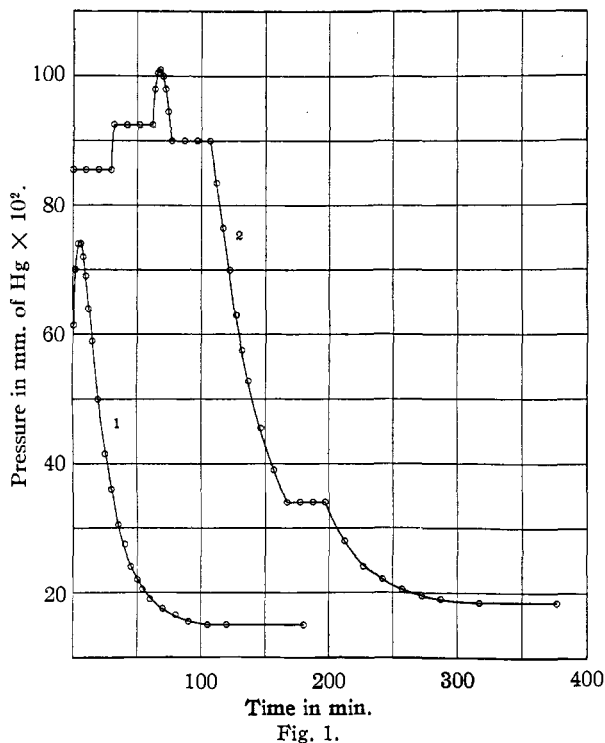counted for merely by a temperature change.   These observations show

Fig. 1.

that in addition to the iridescent deposit, we also had a substance, prob-
ably ethane, which tended to condense near liquid-air temperature at
these pressures.

   Reaction of Ethylene and Hydrogen.—Table II records the results
of several experiments with mixtures of hydrogen and ethylene at varying
pressures.   The data of this table are plotted in Figs. 2 and 3.   In these
runs in which hydrogen always was in excess no noticeable deposit was
formed on the quartz surface.   A glance at the curves will show that the
hump due to the decomposition of the ethylene has been eliminated.   In

TABLE II

REACTION OF ETHYLENE AND HYDROGEN

Time of illumination, min.	Total pressure in mm. of Hg Run					
	3	4	5	6	7	8
0	8.40	8.38	11.80	6.16	3.18	1.50
2	8.28	8.24	11.66	6.08	3.12	1.465
4	8.16	8.12	11.56	6.00	3.06	1.415
6	8.04	8.00	11.44	5.88	2.98	1.36
8	8.00	7.96	11.36	..	2.90	1.30
10	7.96	7.94	11.24	5.66	2.82	1.25
12	..	..	11.12	..	..	1.21
15	7.92	7.90	10.88	5.32	2.60	1.16
20	..	..	10.52	5.02	2.44	1.105
25	..	7.86	10.16	4.78	2.36	1.07
30	7.88	..	9.80	4.58	2.28	1.045
35	..	..	9.42	4.44	..	1.02
40	..	7.86	9.08	..	2.20	1.01
45	..	..	8.80	4.28	..	..
50	..	..	8.56	..	..	0.985
55	..	..	8.38	..	..	..
60	7.90	7.86	8.26	4.16	2.16	.975
70	..	..	8.06	..	..	..
75	..	..	...	..	..	.97
80	..	..	7.94	..	..	..
90	7.90	..	7.88	4.12	2.16	.97
105	..	..	7.84	..	..	..
120	..	..	7.80	4.12	..	..
150	..	..	7.78	..	..	..
180	..	..	7.78	..	..	..
Initial pressure of H_2	7.90	7.88	7.83	4.12	2.15	.975
Initial pressure of C_2H_4	0.50	0.50	3.97	2.04	1.03	.525

Runs 5 to 8 there is a slight change of slope near the beginning of the reaction, showing that the effect is still there. Runs 3 and 4 in which the hydrogen is present in very large excess do not show this change of slope. In all cases the final pressure is equal to the original hydrogen pressure. The absence of a reaction when the 2563 Å. line was absent was demonstrated as before by permitting the arc to heat up. In spite of this small change of slope mentioned above, these data show conclusively that the initial rates of reaction are proportional to the square root of the hydrogen pressure. It is, therefore, obvious that we cannot be dealing with the reaction as ordinarily written, $C_2H_4 + H_2 = C_2H_6$. We are measuring one step, the slow step in a series of reactions and this slow reaction must involve atomic hydrogen to the first power. Professor Bray suggested that this might be the velocity of diffusion of atomic hydrogen formed near the quartz window and this explanation seems the more reasonable since R. W. Wood[7] has shown that 0.5 mm. of mercury

[7] Wood, "Researches in Physical Optics," Columbia University Press, 1913, Part I, p. 54.

vapor at a pressure of 0.001 mm. absorbs two-thirds of the incident light of this particular wave length. At the temperature of our furnace, 45°, the pressure of the mercury vapor is nine times that with which Wood was working and as the absorption approximately follows Beer's law the effective depth for two-thirds of the resonance radiation must be of the order of 0.05 mm. Our primary reaction, therefore, must be $Hg^* + H_2 = Hg + 2H$ + kinetic energy.[7a] The resonance of the mercury atom corresponds to 4.9 volts. Olson and Glockler[8] have shown that the dis--
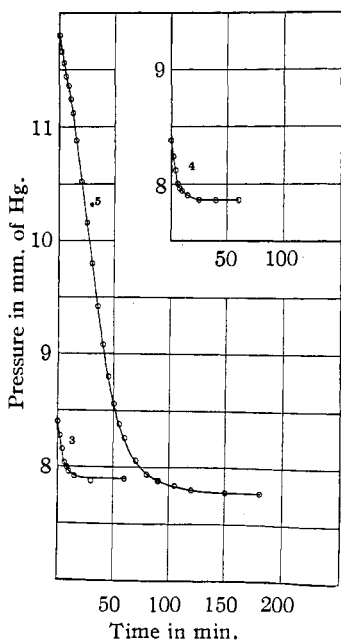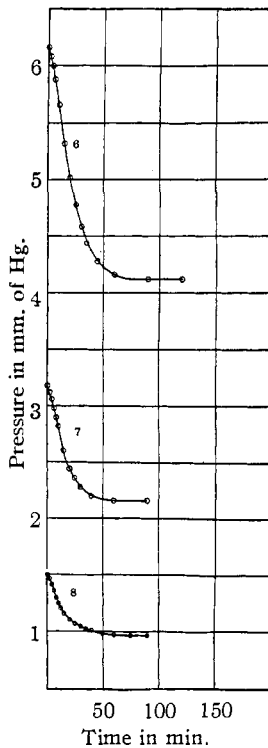

Fig. 2.

Fig. 3.

sociation of hydrogen is about 3.1 volts. The energy which the resonated mercury atom contains in excess over that which is required to dissociate the hydrogen is divided between the mercury and the hydrogen according to the law of momenta. It is, therefore, evident that the atomic hydrogen must diffuse away from this region in which it is formed. If all the following reactions in the formation of ethane are fast as compared to this diffusion then it is evident that this diffusion is the step which determines the rate of the pressure drop.

[7a] The sign (*) is used to denote an atom in the resonated state.

[8] Olson and Glockler, *Proc. Nat. Acad. Sci.*, **9**, 122 (1923).

Fortunately in the researches mentioned above we have some additional information concerning the mechanism which we are proposing. We refer particularly to the paper by Mitchell[5] on the reaction of hydrogen and oxygen and to a paper by Loria[8a] on indirectly excited fluorescence spectra. Mitchell measured the rate of formation of water from a mixture of hydrogen and oxygen in the presence of mercury vapor and the resonance radiation. He showed that the admixture of an inert gas like argon decreased the rate of reaction. Loria on the other hand following up the work of Donat[9] on the excitation of the thallium spectra by excited mercury atoms in the presence of inert gases found as Donat did, that the admixture of an inert gas like nitrogen or argon increased the rate of reaction. Whatever explanation is advanced must, therefore, account for these two apparently contradictory results. Loria, indeed, did consider diffusion of gases from one part of his apparatus to another, and satisfied himself that he had eliminated such diffusion by simplifying his apparatus to one single tube which could be kept at a uniform temperature. However, in the reaction which he was considering, $Tl^* = Tl + h\nu$, we must consider diffusion of resonated thallium atoms. Since these can be formed only in the front part of the tube and disappear in any part of the tube, it is obvious that there can be no equilibrium with respect to them. The diffusion of the activated atoms from the fore end of the reaction chamber does indeed explain all the phenomena observed. The addition of an inert gas retards the diffusion of the activated atoms. Thus in the experiments of Mitchell with hydrogen and oxygen, the action of argon is such as to prevent the hydrogen atoms from leaving the region in which they are formed and also to prevent diffusion of oxygen into this region. The chance, therefore, of the hydrogen atom reacting with an oxygen molecule is small and the chance of two hydrogen atoms recombining to form a molecule is large compared to the corresponding chances when the inert gas is absent. In the experiments with thallium fluorescence the inert gas operates to prevent the diffusion of the excited thallium atom away from the region of formation and, therefore, the re-emission of the energy occurs nearer the point of observation (front part of the tube) with a corresponding increase of the intensity of the light. Our rate of reaction which was dependent on the square root of the hydrogen pressure seems to conflict with the measurements of Stuart[10] on the percentage of collisions of the second kind between mercury and hydrogen. A detailed discussion of this point will be reserved until we have extended our rate measurements over a greater pressure range for the hydrogen.

If these explanations are correct, only the small amount of ethylene

[8a] Loria, *Phys. Rev.*, **26**, 573 (1925).

[9] Donat, *Z. Physik*, **29**, 345 (1924).

[10] Stuart, *Z. Physik*, **32**, 262 (1925).

or hydrogen which is in, or comes into the small volume at the front end of the tube can react directly with the mercury. We have shown that when ethylene reacts directly with the mercury it does so with an initial increase of pressure. Therefore, since at the beginning of the run we have a uniform distribution of both ethylene and hydrogen, it necessarily follows that a small amount of ethylene must react with an increase of pressure. This increase is superimposed upon the decrease due to the hydrogen reaction. This is the explanation of the small change in reaction rate after the first few minutes of each run. It now becomes evident that any increase in the reaction volume or any increase of the rate of diffusion of the ethylene into the reaction volume, must serve to emphasize such a change in rate. To test this a second set of experiments has been performed in which the reaction chamber was freed from liquid mercury. The mercury pressure was then determined by placing the globule of mercury in the trap which was kept at a temperature of 0° and an arrangement for circulating the reacting gases was introduced. These experiments, which will be reported more fully in a later paper, showed definitely an increase in the decomposition of the ethylene.

Summary

It has been shown that ethylene decomposes and polymerizes and a mixture of hydrogen and ethylene reacts to form ethane under the action of resonated atoms. The rate of ethane formation has been shown to be proportional to the square root of the hydrogen pressure. A mechanism for the reaction has been proposed and the results of other investigations have been correlated by means of the proposed mechanism.

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MELTING POINTS OF BARIUM, STRONTIUM AND CALCIUM OXIDES[1]

BY EARLE E. SCHUMACHER

Introduction

A search of the literature reveals the fact that there are no accurate data on the melting points of barium and strontium oxides, and but few recent data on calcium oxide. Among the earliest investigators, E. D. Clarke[2] found that barium oxide fused when heated in the oxyhydrogen

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[1] This investigation is being extended to include the binary system barium oxide-strontium oxide. Preliminary results indicate that the method described in this paper is as satisfactory for the mixtures as for the single components. The results of this work will be published at some later date.

[2] Clarke, *Ann. Phil.,* **8**, 257 (1816).