[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE RATE OF REACTION BETWEEN ETHYLENE AND BROMINE

BY T. D. STEWART AND K. R. EDLUND

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Introduction

Many attempts have been made to ascribe to addition processes very definite mechanisms.

Nef[1] postulated a dissociation or "opening" of the double bond, wherein a tautomeric equilibrium existed between the "open" or reactive form and the closed or unreactive form. Other investigators[2] have assumed that unsymmetrical ethylene derivatives exist in more than one form (excluding cis-trans isomerism) and explain thereby the production of more than one substance on the addition of hydrogen bromide or hypochlorous acid. Nef assumed that but one of the tautomers reacted.

The conceptions of Thiele[3] have been merged with those of Nef by Reich,[4] who has assumed a preliminary addition product, followed by the production of unsaturated valences, to explain trans addition to double bonds.

The type of tautomerism assumed by Nef may be expressed as follows in the notation used by Lewis.[5]

$$\begin{array}{ccc} \text{II} & \text{I} & \text{III} \\ H_2\underset{\cdot}{C}:\underset{\cdot}{C}H_2 & H_2C::CH_2 & H_2\underset{\cdot\cdot}{C}:CH_2 \end{array}$$

where I represents the "closed" double bond and II and III types of "open" double bonds.

Considering a reaction with bromine, if but one of these hypothetical tautomers (present in small amount) reacts with bromine, the following results might be expected: (1) a monomolecular reaction, the rate of which depended on the rate of the tautomerism, if the specific reaction rate with bromine were much faster than the tautomerism; (2) a bimolecular reaction, if the tautomerism were rapid compared to the reaction with bromine.

If all the tautomers could react, at different specific reaction rates, we might expect: (1) a rapid initial reaction, followed by a slower bimolecular reaction, if a small amount of a very reactive tautomer existed and the tautomerism were very slow; (2) a bimolecular reaction, if the tautomerism were rapid compared to the reaction with bromine; and (3) a deviation from either a mono- or bimolecular reaction, if the tautomerism were slow compared to the rate of the reaction of the most reactive tautomer with bromine. An abnormality in the initial phase of the reaction or a deviation from a bimolecular reaction could be explained on the basis of such a tautomerism.

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[1] Nef, THIS JOURNAL, **26**, 1555, 1567 (1904); **30**, 649 (1908).

[2] See, for instance, Stieglitz, *ibid.*, **44**, 1298 (1922).

[3] Thiele, *Ann.*, **306**, 92 (1899).

[4] Reich, *Ber.*, **46**, 3731 (1913).

[5] Lewis, THIS JOURNAL, **38**, 779 (1916). See also Eastman, *ibid.*, **44**, 442 (1922) and Huggins, *ibid.*, **44**, 1608 (1922).

Plotnikow[6] studied the rate of addition of bromine to ethylene in ligroin solution at low temperatures. At —98° he observed what appeared to be a very rapid reaction, lasting from 10 to 20 minutes, followed by a slow bimolecular reaction lasting for several hours. He was not able to give a satisfactory explanation of the initial disturbance. Sudborough and Thomas[7] observed a similar phenomenon when 5-phenyl-Δ,2-pentenoic acid ($C_6H_5CH_2—CH_2—CH=CH—CO_2H$) was treated with bromine in the dark. In this case a small amount of bromine was used up rapidly, and then the reaction practically stopped until exposed to the light. Other investigators[8,9,10,11] report that the addition of bromine to ethylene derivatives in solution is in general a bimolecular reaction, but that the actual rate depends not only on the composition of the compound, but also on the solvent and the presence of acids and salts, iodine, water, etc. It would appear that these reactions are peculiarly susceptible to catalysis, especially by light.

The Reaction Between Ethylene and Bromine

Ethylene was chosen for this study to eliminate the possibility of cis-trans isomerism, and in order to work with gases which would allow more rapid mixing and sampling of the constituents. The intention was to determine the order of the reaction and whether or not any deviation occurred in the initial phase of the reaction. It was found possible to mix completely, in less than 1 second, 2 air streams at 0°, one containing a known amount of ethylene, the other a known amount of bromine, and compare the rate of the reaction during the first 12 seconds with the subsequent rate.

No abnormality exists in the initial phase of the reaction which involves more than 1% of the ethylene. It is believed that no abnormality exists with less than 1%.

The rate of the complete reaction is proportional to the concentrations of both ethylene and bromine. It is also proportional to the surface-volume ratio of the containing vessel. Very little, if any, reaction takes place in the gas phase, even in the presence of water vapor. With a constant surface, the reaction rate is proportional to the concentrations of both ethylene and bromine, and no evidence was obtained of a monomolecular reaction or any deviation from a bimolecular reaction. In the presence of water vapor the catalytic effect of the glass surface is no longer constant as the reaction proceeds.

The surface catalysis could be accounted for by the assumption of adsorbed ethylene or bromine, or both. Whether the adsorption of the ethylene or bromine were the determining factor, there would appear to be no form of gaseous ethylene present in appreciable amounts sufficiently

[6] Plotnikow, *Z. physik. Chem.*, **53**, 605 (1905).

[7] Sudborough and Thomas, *J. Chem. Soc.*, **97**, 2450 (1910).

[8] Sudborough and Thomas, *ibid.*, **97**, 715 (1910); *Proc. Chem. Soc.*, **26**, 294 (1910).

[9] Herz and Myline, *Ber.*, **39**, 3816 (1906); **40**, 2898 (1907).

[10] Barrett and Lapworth, *Proc. Chem. Soc.*, **23**, 18 (1907).

[11] Hofmann and Kirmreuther, *Ber.*, **42**, 4481 (1909).

reactive to combine with gaseous bromine. If the reaction of ethylene takes place through a dissociation or opening of the double bond, such a change does not take place appreciably in the compound *of itself*, but rather under the influence of a surface or solvent. Therefore, the assumption of any dissociation of ethylene, particularly in the gaseous form, appears to be unnecessary.

Experimental Part

Preparation of Materials.—The ethylene was prepared from freshly distilled ethylene dibromide and zinc dust suspended in 80% alcohol. It was purified by passage through 2 coil scrubbers of absolute alcohol at —10°, and stored over water.

The bromine was distilled first from potassium bromide and zinc oxide, and then from phosphorus pentoxide, the middle fraction being taken.

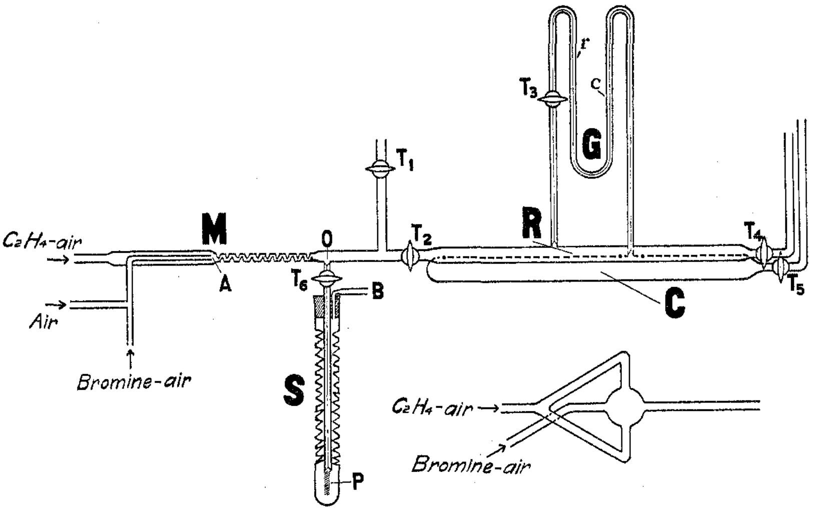

Fig. 1.

Fig. 2.

Apparatus.—A portion of the apparatus used is shown in Fig. 1. Two streams of air of known rates of flow and known content of ethylene and bromine, respectively, came in contact at A and were mixed thoroughly in passing through the baffle tube. At O a sample of the mixed gases could be aspirated and analyzed.

The tube R, with a manometer attached, was used to measure the rate of the reaction. It was filled with the reacting gases by allowing the stream to sweep through it, and at any desired time the stopcocks T_2 and T_4 were closed simultaneously with the opening of T_3 and closing of T_5. At this time the pressure in R and C was the same (atmospheric), and any subsequent change in the manometer was a measure of the reaction, $C_2H_4 + Br_2 = C_2H_4Br_2$, since the reaction proceeds with a decrease in the number of moles of gas and, therefore, with a decrease in pressure in a vessel of constant volume. The manometer liquid used was pure α-bromonaphthalene, the density of which was found to be $^1/_{9.217}$ that of mercury at the working temperature. The volumes of the tubes R and C changed slightly with the change in level of the manometer liquid, for which a correction was applied. The reaction was not measured beyond the point at which the vapor pressure of ethylene dibromide was reached,[12] and in later experiments, in which the bromine concentration was about 2.0 mm. the reaction was allowed to go to completion and the bromine concentration at zero time (time of closing T_4 and T_5) taken as the total decrease in pressure. The stopcocks T_3 and T_6 were lubricated with phosphorus pentoxide and protected from the ice-bath by rubber thimbles.

All experiments were carried out in a water thermostat, which was maintained at a constant temperature between 0.05° and 0.15°. The actual temperature depended on the fineness of the ice packed about a stirrer, but for any one experiment the temperature was constant and uniform to 0.02° and within the above limits. No ice was allowed near the tubes R and C.

The ethylene-air mixture of about the desired concentration was stored in a large bottle and displaced by a jet of water under constant pressure head insuring a constant rate of flow. The stream (about 400 cc./min., measured by a flow-meter) was purified by passage over calcium chloride, solid potassium hydroxide and phosphorus pentoxide, and a sample for analysis could be withdrawn just before entering the mixing chamber M. The drying tube, flow-meter, and a copper coil to insure cooling, were placed in the thermostat.

The bromine was placed in a pair of Washburn saturators (placed in the thermostat) which were continually rocked during an experiment and connected to the rest of the apparatus by glass springs. A slow stream of air (30–50 cc./min.) was generated by displacement from a small bottle by a jet of water under constant head, dried, and passed through the saturators. The rate of flow was obtained from the rate of flow of the jet, and correction made for the water vapor removed and the cooling to 0°, since the bottle and jet were in a separate thermostat of tap water. The concentration of bromine at the point A was calculated from the vapor pressure[13] at that temperature and the rate of flow of the various gas streams. Since it was desirable to have the 2 streams at A of about the same linear velocity, a measured stream (300 cc./min.) of dry air was introduced into the bromine as shown, and the orifices of the mixing chamber were made of nearly equal cross section. To introduce water vapor into the reaction, the drying tubes were omitted from this third stream.

Fig. 2 illustrates a form of mixing chamber which was found to pocket badly at the entrance tube of the bromine.

Several blank runs, using air instead of ethylene, and analyzing the gas at O, showed that the initial bromine concentration could be calculated to 0.01 mm. of mercury. A sample drawn from the same gas mixture at the end of the apparatus showed the same concentration of bromine as at O, indicating that mixing was complete at O.

Sampling and Analysis.—Measured samples (600–900 cc.) were aspirated at O through T_6 and B. The calibrated aspirator bottle was outside the bath, and correction was made for changes in temperature and for water vapor in calculating the actual volume withdrawn. Each sample was analyzed for bromine and ethylene. The sampler S was a hard glass test-tube, baffled as shown, so that the glass capillary carrying

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[12] The vapor pressure of ethylene dibromide is given by Regnault, *Mém. Acad. Paris*, **26**, 462 (1862), as 3.92 mm. at 0°. Some early results indicated that this was too high, and a redetermination was made by Mr. S. Ruby under the direction of Dr. W. M. Latimer of this Laboratory. Using the method of W. M. Dehn [THIS JOURNAL, **29**, 1052 (1907)], Mr. Ruby obtained the values 1.9 mm., 2.1 mm., 2.0 mm., in three experiments.

[13] Ramsay and Young, *J. Chem. Soc.*, **47**, 48 (1885); **49**, 453 (1886). Isnardi, *Ann. Physik*, **61**, 264 (1920). The mean of the values given by these investigators was used, and was taken as 66.0 mm. at 0°. The change with the temperature was taken as 3.0 mm. per degree.

a coil of platinum wire P made a tight fit. A solution of pure potassium iodide filled the free space at the bottom, and it was possible to take a sample at the rate of 400 cc./min. with complete absorption of bromine and no detectable loss by spray. The iodine liberated was titrated with 0.025 *N* thiosulfate solution and the result expressed as millimeters of mercury pressure at the point of sampling. The length of time which the gases were in the sampler depended on the rate of sampling, and at 400 cc./min. is estimated to be about 0.1 second, of which about $^1/_4$ was spent in the fine capillary tube and the remainder in the connecting stopcock and tube.

Determination of Initial Concentrations

The concentration of the bromine and ethylene at the point A could be calculated as described above, for the concentrations used, to within 0.5%.

The concentration of bromine in the tube R at zero time (first reading of the manometer) was determined by extrapolation of the curves (Fig. 3) showing the decrease in pressure with the time, to infinite time, and taking the total decrease in pressure as the initial concentrations of bromine. Ethylene was always in excess and the analysis at the point O was sufficiently accurate for its concentration.

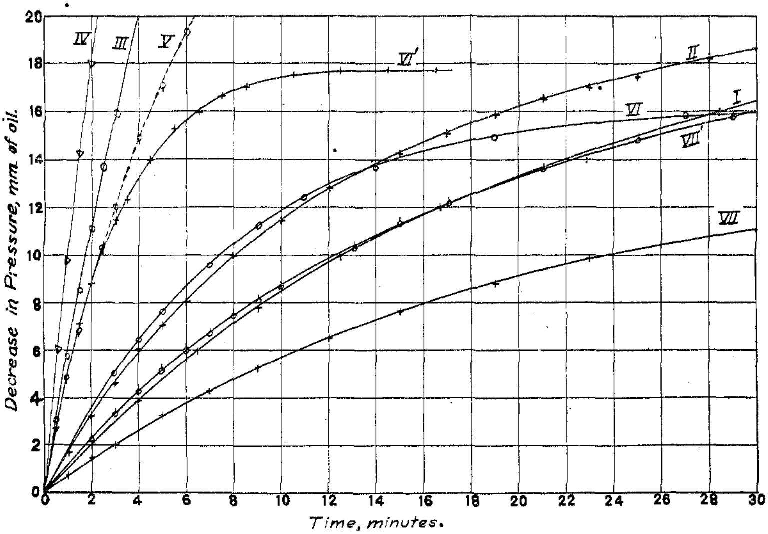

Fig. 3.—Rates of reaction between ethylene and bromine gases (Table VI).

The concentrations of bromine as determined at the point O by sampling and analysis could not be used, due to a rapid reaction in the moist capillary tube, but for Expts. 1 and 2 they had to be used as an approximation, since the bromine concentration was greater than the vapor pressure of ethylene bromide and the reaction could not be allowed to go to completion. Hence these concentrations may be in error by as much as 10%, and are probably too low as given.

Experimental Results

The Initial Phase of the Reaction.—An approximate idea of the rate of the reaction during the first 12 seconds can be obtained from Table I. The reacting gases were in the mixing chamber (A to T_2, Fig. 1) for less than 1 second of this time and for the remainder in the tube R. Col. 2 gives the calculated initial concentration of bromine at the point A, and Col. 3 the concentration of bromine about 12 seconds later, which was zero time as plotted for the remainder of the reaction in Fig. 3. All concentrations are in millimeters of mercury. Excluding Expt. 7, this represents a reaction from 3 to 7 times as fast as the reaction in the succeeding 12 seconds as taken from the corresponding curves in Fig. 3. Experimental difficulty in Expt. 7 caused an unusually large error, and the decrease noted in the other experiments may be in error (probably high) by 0.05 to 0.08 mm.

TABLE I

THE APPROXIMATE RATE OF REACTION AND THE PERCENTAGE OF ETHYLENE REACTING DURING THE FIRST TWELVE SECONDS

Expt.	Br_2 at A	Br_2 in R	Decrease	C_2H_4 in R	% C_2H_4 used up
6	2.05	1.77	0.28	15.0	1.8
6′	2.28	1.92	0.36	15.5	2.3
7	2.03	1.69	0.34	4.83	7.0
7′	1.97	1.80	0.17	4.78	3.5

This rapid initial reaction was due to catalysis of the reaction by the walls of the mixing chamber. That this could be true was shown by attempts to measure the initial concentrations of the reacting gases by sampling at O (Fig. 1). In the few tenths of a second that the gases were in the sampling tube an amount of bromine was used up which corresponded to a reaction at least 100 times as fast as a reaction in a dry 2cm. tube (Curve II, Fig. 3). The apparent reaction rate depended on the rate of sampling. This was shown by introducing a second sampler, similar to the first, between O and T_2 (Fig. 1), so that 2 samples of the same mixture could be withdrawn at different rates. The results of two experiments are shown in Table II, where P′ is the point in the second sampler corresponding to P in the first. The bracketed figures were calculated as described in the previous section. Concentrations are expressed in mm. of mercury.

TABLE II

THE EFFECT OF THE RATE OF SAMPLING ON THE DETERMINATION OF THE CONCENTRATIONS OF THE REACTING CONSTITUENTS

	Experiment I			Experiment II		
	Initial (at A)	First sample (at P)	Second sample (at P′)	Initial (at A)	First sample (at P)	Second sample (at P′)
C_2H_4 conc...	(10.9)	10.71	8.82	(8.40)	7.87	(7.78)
Br_2 conc.....	(3.10)	2.87	0.99	(2.90)	2.41	2.32
Rate of sampling......	....	495 cc./min.	63 cc./min.	....	225 cc./min.	200 cc./min.

The drop in the concentration of the bromine was roughly proportional to the rate of sampling, showing that most of the reaction took place in the sampling tube and was enormously faster than the reactions in larger tubes. It would appear that the rapid initial reaction found in Expts. 6, 6′ and 7′ was entirely due to the small mixing chamber, and cannot be ascribed to the presence in small amount of any abnormally reactive substance. To make more certain of this, in several experiments the excess ethylene was collected and used again within an hour. In other experiments, the ethylene was treated with bromine (about 10%) 1 minute before it entered the mixing chamber. The same rapid reaction in the sampling tubes was always observed with this pre-treated ethylene.

These experiments show that there is no abnormality in the initial phase of the reaction between ethylene and bromine which involves more than 1% of the ethylene.

The Complete Reaction. Catalysis by Surfaces.—The results of the previous section indicated a marked catalysis of the reaction by glass surfaces and water. A series of experiments was made to determine whether or not any appreciable amount of the reaction took place in the gas phase, the effect of water, and whether any evidence of tautomeric forms of ethylene could be obtained by varying the relative concentrations of bromine and ethylene.

The static method used to follow the course of the reaction has been described. The conditions attending each experiment are given in Table III. Col. 2 gives the diameter of the tube R (Fig. 1), Col. 3 the approximate ratio of surface to volume, and Cols. 6, 7, 8 and 9 the concentrations of ethylene and bromine in the tube R at the initial reading of the manometer. In Col. 4 the term "dry" indicates that all gases had been passed over phosphorus pentoxide; "wet" indicates the presence of water vapor pressure equivalent to about 1.5 mm. of mercury in the gas stream. In Col. 5 the term "dry" indicates that the tube R had been swept out for 1 to 2 hours at room temperature with air dried over phosphorus pentoxide before the experiment; the term "wet" indicates the same conditions as in Col. 4. The experiments are numbered in the order in which they were performed, and in Expts. 1, 2, 3 and 4 the walls were air-dried, without special care. The results of these experiments (Fig. 3) show that the walls must have been wet, comparatively, in Expts. 3 and 4, since the reactions resembled the rapid reactions of Expts. 5, 6′, and 7′ in which water was present. These two experiments are not further considered, and are cited only to show the necessity of preparing the glass surface if consistent results are to be obtained. It seems justifiable to compare the results of Expts. 1 and 2 with later "dry" runs, since they are not obviously "wet," and are in agreement with each other, although the walls doubtless contained more moisture than those of Expts. 6 and 7. The bromine concentration of Expt. 5 could not be determined, due to an accident, but its partial pressure was probably equivalent to about 35 mm. of oil. Blank runs using water vapor in air alone, and bromine vapor in air alone showed that in the time of the experiments no change in pressure other than that due to the reaction was sufficient to cause appreciable error.

TABLE III

THE EXPERIMENTAL CONDITIONS ATTENDING EXPTS. 1–9, CORRESPONDING TO CURVES I–VII IN FIG. 3 AND RESULTS GIVEN IN TABLES IV AND V

	Dimensions of tube				Initial concentrations			
					Br_2		C_2H_4	
Expt.	Diameter Cm.	s/v	Conditions Gases	Walls	Mm. of oil	Mm. of Hg	Mm. of oil	Mm. of Hg
1	2	2	dry	...	31.5	3.42	44.1	4.78
2	2	2	dry	...	24.3	2.64	101.8	11.0
3	1	4	dry	...	34.8	3.78	105.4	11.4
4	1	4	dry	...	36.8	3.99	88.9	9.6
5	1	4	wet	wet	..	..	85.0	9.2
6	1	4	dry	dry	16.3	1.77	138.5	15.0
6′	1	4	wet	wet	17.7	1.92	143.0	15.5
7	1	4	dry	dry	15.6	1.69	44.5	4.83
7′	1	4	wet	wet	16.6	1.80	44.0	4.78
8	4	1	dry	dry	13.5	1.46	200.0	21.7
9	4	1	dry	dry	14.0	1.52	180.0	19.5

The results of the experiments in the 1- and 2cm. tubes are given in Fig. 3 and Table IV. Unimolecular constants have been calculated, assuming the reaction proportional only to the concentration of the ethylene, expressed in millimeters of oil. For no one run is this a constant, and for different runs in the same tube, where the ethylene concentration is varied, there is no agreement.

TABLE IV

UNI- AND BIMOLECULAR CONSTANTS CALCULATED FOR THE REACTIONS IN THE 1 AND 2CM. TUBES

Expt.	1		2		6		6′		7		7′	
Time interval Min.	$K_1 \times 10^4$	$K_2 \times 10^4$	$K_1 \times 10^4$	$K_2 \times 10^4$	$K_1 \times 10^4$	$K_2 \times 10^4$	$K_1 \times 10^4$	$K_2 \times 10^4$	$K_1 \times 10^4$	$K_2 \times 10^4$	$K_1 \times 10^4$	$K_2 \times 10^4$
0–1	232	7.6	168	7.17	131	8.53	355	22.0	175	11.4	246	15.5
1–2	...	...	161	7.39	...	9.39	...	..	...	10.7	276	18.5
2–3	231	8.1	137	6.84	113	9.57	237	29.2	136	9.7	...	..
3–4	...	...	...	..	103	9.86	127	..	...	11.4	226	17.6
5–6	215	8.1	107	6.59	...	10.0	55	26.4	...	10.7	205	18.7
7–9	194	7.87	...	6.85	62	10.7	...	..	126	11.6	197	20.1
15–19	...	...	...	..	19	10.1	...	..	108	11.0	125	28.5
Av.		7.9		6.8		9.7				10.9		

Bimolecular constants have been calculated, expressing the concentrations of ethylene and bromine in millimeters of manometer oil. The agreement for any one "dry" run is very good, and for different runs in the same tube the agreement is within the experimental error. For the "wet" runs there is more divergence. It would appear that the "dry" glass surface is fairly reproducible and constant, since the "wet" Expt. 6′ was made between the two "dry" Expts. 6 and 7, necessitating a drying of the tube, and also since for this condition the bimolecular reaction holds. In view of these facts it would appear possible to consider the bimolecular constant a means of comparing the rate of the reaction in tubes of different surface-volume ratio.

The results of the experiments in the 4cm. tube are given in Table V. In these cases the tube was not filled by displacement, but by evacuating and then drawing in the mixed gases during the course of 30–40 seconds. The manometer readings were plotted as usual against the time, and the curve extrapolated to obtain the total pressure drop at the completion of the reaction. A blank run with air only showed that this method of filling the tube resulted in a cooling of the gas so that the pressure increased 3.5 mm. of oil instead of remaining constant, and 5 minutes was required for it to come to the temperature of the thermostat. Therefore the first 6 minutes of these runs were disregarded, and the initial bromine concentration taken as the total decrease in pressure after that time.

Table V

Experiments in the 4cm. Tube

Expt. 8				Expt. 9			
Time Min.	Br_2 concn. Mm. of oil	C_2H_4 concn. Mm. of oil	$K_2 \times 10^4$	Time Min.	Br_2 concn. Mm. of oil	C_2H_4 concn. Mm. of oil	$K_2 \times 10^4$
0	13.54	200.0	...	0	14.01	180.0	..
1	12.44	198.9	4.2	1	13.26	179.2	3.06
2	11.44	197.9	4.1	2	12.69	178.7	2.47
3	10.58	197.0	3.9	4	11.59	173.6	2.54
4	9.74	196.2	4.2	6	10.69	176.7	2.28
5	8.99	195.4	...	9	9.24	175.3	2.78
6	8.28	194.7	4.2	11	8.40	174.4	2.72
7	7.68	194.1	...	13	7.65	173.6	2.69
9	6.56	193.0	4.1	17	6.54	172.5	2.26
13	4.79	191.2	...	20	5.59	171.6	3.04
19	3.02	189.5	4.0	28	4.42	170.4	1.66
..	..	...	...	35	3.46	169.5	2.06
..	..	...	...	41	2.63	168.6	2.70
..	..	...	...	48	2.02	168.0	2.25
Av.			4.1				2.50

The results of the experiments in the 1- and 2cm. tubes indicated that there was possibly some gaseous reaction, but the very slow reaction in the 4cm. tube showed beyond doubt that the reaction was largely a surface one. If the rate of the reaction is proportional to the surface in a cylindrical tube it should be inversely proportional to the diameter, neglecting the ends of the tubes. The excellent agreement with this assumption of the values for K_2 in Expts. 6, 7 and 8,9 is somewhat fortuitous, since there can be no assurance that the wall conditions were identical, but since no more care was exercised to remove water from the 4cm. tube than in Expts. 6 and 7, the results are believed to be comparable.

In addition to this quantitative evidence that the rate is proportional to the surface and, therefore, entirely a surface reaction, we have the evidence of the heat of the reaction. When the research was first planned, it was thought possible to work under such conditions that the heat of the reaction would not interfere. This is given by Berthelot as +27,200 cal. per mole for the reaction, $C_2H_4 + Br_2$ (gas) $= C_2H_4Br_2$ (gas). Assuming a rate for the reaction as in Expt. 9, about 2.9 calories were produced in the first minute per 22.4 liters of the reacting mixture, and had none of this heat been lost this would have produced a rise in temperature of about 0.4°, or a rise in pressure of about 10 mm. of the manometer oil. Since, in the experiment cited, longer than 5 minutes was required to equalize a temperature difference which caused a pressure change of 3.5 mm., it seems obvious that the heat of the reaction must have been lost to the walls as fast as produced, which is conceivable only for the surface reaction. These considerations in connection with the very rapid reactions of Expts. 3, 4 and 6′ would lead to the conclusion that not more than 2% of the reaction took place in the gas phase, if any.

It might be expected that water would displace adsorbed bromine or ethylene on the surface, and that the faster reaction in these cases (6′ and 7′) was due to a gaseous reaction brought about by the water vapor. That this cannot be the case is shown by the above considerations concerning the heat of the reaction.

Table III gives the maximum amount of bromine which could have been present and the amount found at zero time by assuming the decrease in pressure to be a measure of the bromine concentration. The difference was taken to be the reaction before zero time. Since this difference is small and reasonable, it appears that no great amount of the reacting gases or product was adsorbed at any given time.

In all of the experiments described above, the reaction tube was exposed (under water) to the light from a 100watt tungsten filament lamp. An experiment was made with the reaction tube covered with bicycle tape and tar paint, using the 1cm. tube. The results indicated a slightly faster reaction than that found in Expts. 6 and 7, showing that the condition of the wall was more important than exposure to this light in its effect on the rate of the reaction.

Summary

The rate of the reaction between gaseous ethylene and gaseous bromine, diluted with air, has been studied. The reaction takes place for the most part, if not entirely, on the walls of the containing vessel. No evidence of a gaseous reaction could be found. The reaction rate is increased by the

presence of water. With a constant surface, the rate of the reaction is proportional to both the concentration of ethylene and concentration of bromine. No evidence of any deviation from a bimolecular reaction was found. The specific reaction rate during the first 12 seconds of the reaction is apparently greater than the subsequent rate, but the abnormality does not involve more than 1% of the ethylene. It is thought that this small initial reaction owes its higher velocity to wall catalysis, and is not to be taken as evidence of a highly reactive form of ethylene present in small amount.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE UTILIZATION OF PARA-DICHLOROBENZENE FOR SYNTHESIS IN THE DIPHENIC ACID SERIES

BY EDWARD B. HUNN[1]

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In the course of an investigation in the Sheffield Chemical Laboratory dealing with certain organic substances which might be expected to exert a pharmacological action similar to that of the alkaloid, morphine, it became necessary to develop a method for synthesizing disubstituted derivatives of diphenic acid with halogen substituents in the 5 and 5′ or the 6 and 6′ positions. These positions in the diphenic acid nucleus correspond to the 3,6 and 4,5 positions in the phenanthrene molecule, which configuration according to our present knowledge is a part of the morphine molecule.

For the synthesis of substituted diphenic acids one has recourse to three general methods, (1) the oxidation of known phenanthrene or phenanthraquinone derivatives, (2) direct substitution in the diphenic acid molecule, and (3) synthesis by bringing together 2 molecules of a substituted benzoic acid. The number of known symmetrically substituted diphenic acids is small. Schmidt[2] has prepared the following by the oxidation of the corresponding phenanthraquinone derivatives; 4,4′-dibromo-, 6,6′-diamino-, 6-amino-, 6′-hydroxy-, 6,6′-dinitro-, 4,4′-diamino-, and 4,4′-dihydroxy-diphenic acids. Direct nitration or halogenation leads chiefly to substitution in the 4 and 4′ positions. By the third procedure Ullmann[3] has prepared 4,4′-dinitro-diphenic acid from 2-iodo-3-nitrobenzoic acid, and Mayer[4] has made 6,6′-dimethyl-diphenic acid from 2-iodo-3-methylbenzoic acid ester.

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[1] This paper is constructed from a dissertation presented by Edward B. Hunn in June, 1921, to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy. (T. B. Johnson.)

[2] Schmidt, *Ber.*, **36**, 3726 (1903); **37**, 3567 (1904); **38**, 3769 (1905).

[3] Ullmann, *ibid.*, **34**, 2174 (1901).

[4] Mayer, *ibid.*, **44**, 2298 (1911).