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

THE KINETICS OF THE REACTION OF HEXAPHENYLETHANE WITH OXYGEN

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Introduction

Gomberg and others have shown that hexaphenylethane when dissolved in non-ionizing solvents such as ether, benzene, toluene and carbon tetrachloride exists in at least two forms, undissociated hexaphenylethane and the free radical triphenylmethyl. The solutions are amber-colored, and it appears to be proved conclusively that the color is due to the free radical, part or all of which may be colored. When the amber-colored solution of hexaphenylethane in these solvents is shaken with air or oxygen, the color decreases very rapidly, the solution becoming colorless if the hexaphenylethane is sufficiently pure. A few moments after the shaking is stopped, the color reappears, but much more slowly than it disappeared. The over-all reaction in this process is

$$(C_6H_5)_3C—C(C_6H_5)_3 + O_2 \longrightarrow (C_6H_5)_3C—O—O—C(C_6H_5)_3$$

This simple experiment suggests that there is some colored substance in the solution before the addition of oxygen which is in equilibrium with hexaphenylethane, and that this substance reacts with oxygen to form triphenylmethyl peroxide at a much faster rate than that of the reaction through which it is in equilibrium with hexaphenylethane.

Again, the color of hexaphenylethane solutions decreases on dilution to a less extent than that predicted by Beer's law.[1] Hence the colored substance is formed by a reversible dissociation.

These two experiments together show that hexaphenylethane dissociates to form a colored substance, triphenylmethyl, whose reaction with oxygen can be much faster than its recombination. When such a condition exists, the kinetics of the over-all reaction are those of the preliminary slower step. Thus in this case the rate of oxidation of hexaphenylethane by this mechanism has to be that of its dissociation and is independent of the concentration of oxygen. That the necessary condition of rapid reaction of triphenylmethyl with oxygen can be achieved may be seen from the following considerations. The color of a hexaphenylethane solution can easily be reduced to less than one-tenth of its original depth by shaking with air or oxygen. Under these conditions the rate of re-combination, a bimolecular reaction, is reduced to less than 1% of its value in the oxygen-free solution, while that of dissociation is presumably unchanged. Consequently, practically all of the molecules which dissociate react with oxygen and very few of them return to the original hexaphenylethane. This failure of the

[1] J. Piccard, *Ann. chim.*, **381**, 347 (1911).

intermediate to return to the original state is the necessary condition that a preliminary step shall be the rate-determining reaction.

It is, therefore, of interest to study the kinetics of the absorption of oxygen by hexaphenylethane solutions, for in this way the rate of the dissociation will be measured, or it will be possible to show that there is some other mechanism for the reaction.

In such measurements it will be necessary that the passage of oxygen from the gas phase to the liquid does not delay the reaction. Therefore, the solutions must be shaken sufficiently vigorously to permit this transfer of oxygen to occur at a rate much faster than that of the oxidation. In our measurements concordant results were obtained over periods during which the rate of passage of oxygen from the gas to the liquid varied thirty-fold. Again, in the beginning of each experiment, while the solvent was being saturated with oxygen and the free radical was being reduced below its equilibrium concentration, the rate of transfer of oxygen across the gas–liquid interface was often two hundred times as fast as the rate of absorption of oxygen at stages of the run during which significant measurements were being made. These two observations, which can be seen by an inspection of the curves in Fig. 1, show that a sufficiently rapid solution of oxygen was achieved. Attempts were made to measure the rate of solution of oxygen in carbon tetrachloride under the conditions of the experiment, but it was found to dissolve too rapidly.

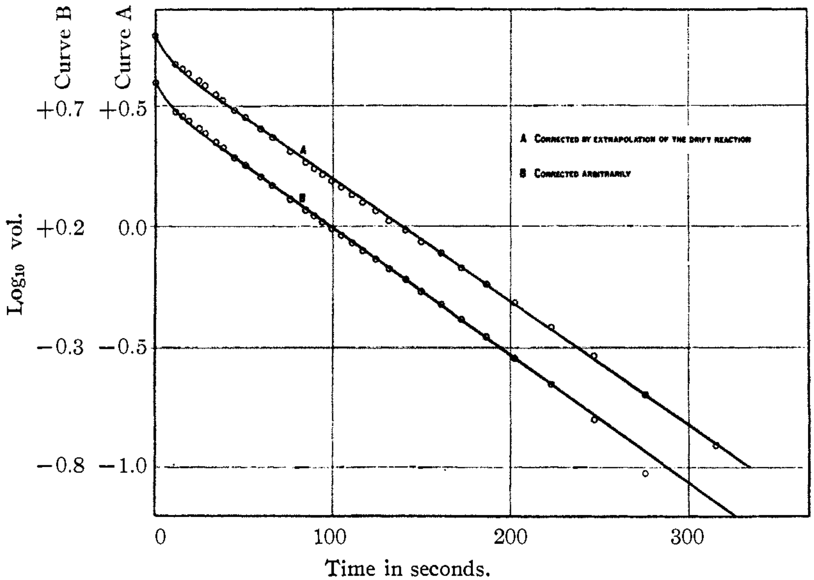

Fig. 1.—The logarithm of the volume of oxygen yet to be absorbed by hexaphenylethane plotted against the time.

The kinetics of the reaction was studied over ranges of temperature, of concentrations of hexaphenylethane and of partial pressures of oxygen. During any one run only the second variable changed. The solvent was carbon tetrachloride throughout. A few experiments were carried out in the presence of some of Bäckström's oxidation inhibitors.

Experimental Method

The method consisted of shaking hexaphenylethane solutions in the presence of oxygen gas mixed with nitrogen and measuring the rate of absorption of the gas.

The reaction was carried out in a vessel connected to a powerful automatic shaker, the whole being immersed in a thermostat. The volume of the containing vessel was so large, compared to that of the gas absorbed, that the composition of the oxygen and nitrogen mixtures used did not change significantly during an individual experiment.

The reaction vessel was attached by a rubber connection to a long calibrated horizontal tube which was bent at the end and dipped into a basin of liquid. This tube served as a constant pressure gas buret.

During an experiment the liquid meniscus advanced along the buret, and as it passed the calibration marks the time was registered. This was done by pressing a key which sent sparks through a paper tape moving at a known and constant rate. After the run had been made, the times were calculated from the distances between the marks burned through the tape.

Owing to its length, the buret was not immersed in the thermostat, but was surrounded by a jacket through which water flowed. In order to have an evenly moving meniscus, water was used as the buret liquid.

A certain amount of difficulty was encountered owing to the violent shaking which caused vibrations of the meniscus in the buret. This trouble was entirely overcome. In its final construction the apparatus could be shaken without causing any appreciable fluctuations of the meniscus in the buret.

A temperature of 0° was maintained in the thermostat by a mixture of ice and water. On account of the excellent stirring no variation in temperature as large as a tenth of a degree could be observed. For temperatures below 0° alcohol was added to the above mixture. In such experiments the temperatures increased a couple of tenths of a degree during the runs. These variations of temperature were measured. The observed volumes of gas were then corrected for this change of temperature from the known volume of gas in the reaction vessel and on the assumption that the change of temperature was proportional to the elapsed time. A few measurements were made above 0°. In these cases no device except insulation was used to keep the temperature of the thermostat constant. The rate of change of the temperature was observed and the necessary corrections to the volumes applied.

The solutions of hexaphenylethane were made by shaking solutions of triphenylchloromethane with molecular silver. The whole process of preparation and siphoning away from the silver chloride into containers was done in an atmosphere of inert gas. These containers were sealed and put into the reaction vessel. The required mixture of oxygen and nitrogen could then be introduced and the whole apparatus allowed to come to temperature equilibrium. When the shaker was started the sealed container was broken and the solution came into contact with the gas. A forward motion of the meniscus showed when this occurred.

Results at Constant Oxygen Pressure and Temperature.—The motion of the meniscus in the gas buret presented three phases, which appeared clearly differentiated to an observer of the experiment. The initial phase was a very rapid advance, that is, absorption of gas, starting the moment the sample tube broke and lasting about ten seconds. The second phase was a slower advance of the meniscus, decreasing in rate as the time increased. The second phase merged gradually into the final phase, which was a very slow advance continuing for more than an hour.

The interpretation of the rapid gas absorption during the initial phase was the process of saturating the carbon tetrachloride with oxygen as well as the reaction of the gas with that portion of the hexaphenylethane which existed at the start as the free radical.

The major portion of gas absorption takes place during the second phase, which represents the main reaction, the oxidation of hexaphenylethane.

The last phase is evidently not due to any reaction of hexaphenylethane, for the apparent half time of the second or main phase is about one minute, so that after ten minutes there should be practically no hexaphenylethane left; but the third phase continues noticeably for over an hour. Further, there is no combination of reactions of different orders but of the same substance which can account for both the second and final phases in the oxygen absorption, if reactions having ridiculous orders are excluded. On the other hand, the entire advance of the meniscus from twenty seconds after the start to the finish can be accounted for on the assumption that there are two substances present, one of which absorbs oxygen by a first order reaction whose half time is a little less than a minute, while the other compound is present in comparatively small quantities and reacts at a much slower rate, the half time of the second reaction being about a quarter of an hour.

In order to be sure that the main reaction is first order with respect to hexaphenylethane, it is necessary to correct for the side reaction. This may be done by extrapolating the measurements obtained during the latter part of the experiment, in order to calculate the absorption of gas by the impurity during the main part of the run.

The procedure is as follows: the experiment is continued until no more oxygen is absorbed, so that the volumes of oxygen yet to be absorbed may be obtained for any time at which a reading is made. The values of the logarithm of this quantity are plotted against the times and the best straight line is drawn through the points obtained ten minutes or more after the start. From the extension of this line to earlier times, the amount of oxygen which will be absorbed by the impurity may be read off. By subtracting this value from the total amount of oxygen yet to be absorbed, the volume of the gas yet to be absorbed by hexaphenylethane is obtained. This quantity is proportional to the concentration of hexaphenylethane. It may be noted that it is assumed that the side reaction is first order. The volumes involved are too small to decide this point, but for that very reason the assumed order is unimportant.

This method may be illustrated by a typical experiment, which was carried out at 0° and with 0.93 atmosphere of oxygen. The absorption of oxygen by the impurity near the end of the run is shown in Table I.

Table I

Absorption of Oxygen by the Impurity

Time in minutes	0	10	15	20	25	30	35	40
Vol. to absorb, cc.	0.670	0.250	0.155	0.147	0.141	0.140	0.135	0.100
Time in minutes	45	50	55	60	65	70	75	80
Vol. to absorb, cc.	0.054	0.043	0.054	0.052	0.052	0.025	0.020	0.011
Time in minutes	85	90	95	100	105	110	115	120
Vol. to absorb, cc.	0.013	0.010	..	...	...	...	...	...

The volumes given in the second and fourth lines are calculated on the basis that the final reading is 6.770. The straight line which was drawn through the plot of the logarithms of these values against time corresponded to a total volume of 0.49 cc. absorbed by the impurity and a rate constant of 0.044 reciprocal minutes.

Other experiments agreed approximately with this one, that is, somewhere between 5 to 15% of the oxygen taken up was absorbed by a reaction whose half-time was approximately a quarter of an hour.

In Table II the first two columns show the times and the volumes of oxygen yet to be absorbed. Column 3 is the extrapolation of lines two and four of Table I. The volumes of oxygen yet to be absorbed by hexaphenylethane are exhibited in the fourth column.

TABLE II

ABSORPTION OF OXYGEN BY HEXAPHENYLETHANE

Time, sec.	Total cc. to be abs.	To be abs. by impurity, cc.	To be abs. by hexaphenylethane, cc.	Same as Col. 4 but obt. by approx. method	Time, sec.	Total cc. to be abs.	To be abs. by impurity, cc.	To be abs. by hexaphenylethane, cc.	Same as Col. 4 but obt. by approx. method
0	6.70	0.49	6.21	6.25	99.2	2.00	0.46	1.54	1.55
11.1	5.19	.49	4.70	4.74	104.7	1.90	.45	1.45	1.45
15.3	4.99	.49	4.50	4.54	110.5	1.80	.45	1.35	1.35
18.9	4.79	.49	4.30	4.34	117.0	1.70	.45	1.25	1.25
24.7	4.49	.48	4.01	4.04	124.0	1.60	.45	1.15	1.15
28.2	4.30	.48	3.82	3.85	131.5	1.50	.45	1.05	1.05
34.0	4.00	.48	3.52	3.55	140.4	1.40	.44	0.96	0.95
38.3	3.80	.48	3.32	3.35	149.4	1.30	.44	.86	.85
44.9	3.50	.48	3.02	3.05	160.9	1.20	.43	.77	.75
50.5	3.30	.47	2.83	2.85	172.3	1.10	.43	.67	.65
59.4	3.00	.47	2.53	2.55	186.1	1.00	.43	.57	.55
65.8	2.79	.46	2.33	2.34	202.0	0.90	.42	.48	.45
76.0	2.50	.46	2.04	2.05	222.5	.80	.42	.38	.35
84.6	2.30	.46	1.84	1.85	245.2	.70	.41	.29	.25
89.5	2.20	.46	1.74	1.75	275.3	.60	.40	.20	.15
93.9	2.10	.46	1.64	1.65	315.0	.50	.376	.124	.05

In Fig. 1, Curve A, the logarithms of the volumes of oxygen yet to be absorbed by hexaphenylethane are plotted against the times. In this figure the curve from twenty-five seconds onward is a ruled line whose slope corresponds to a rate constant equal to 0.0118 reciprocal seconds. It can thus be seen that the reaction is quite strictly first order with respect to hexaphenylethane over a thirty-fold change of the concentration of that substance.

This method of calculating the rate constant was carried out for several runs at 0°, but it could not be used at other temperatures, because the thermostat could not be held sufficiently constant in temperature to permit an approximate evaluation of the effect of the side reaction; therefore, another method of correction was used. This was based on the knowledge previously obtained that the main reaction is strictly first order with respect to hexaphenylethane.

This second way of correcting for the side reaction consists of subtracting such a constant amount from the observed values of oxygen yet to be absorbed, that their logarithms fall on a straight line when plotted against the time. Thus in the experiment shown in Tables I and II, if 0.45 cc. is subtracted from the amounts of oxygen yet to be absorbed, the resulting values, which are shown in Col. 5 of Table II, are such that their logarithms when plotted against the time fall on a straight line from about 25 to 220 seconds. This can be seen on inspection of Curve B of Fig. 1. In this drawing the curve from twenty-five seconds onward is a ruled line whose slope corresponds to a rate constant of 0.0122 reciprocal seconds. This value agrees fairly well with 0.0118, obtained by the logically more correct first method.

The second method is only applicable when the drift reaction contributes only a small fraction to the rate of absorption of oxygen. Thus in the present experiment between the times 50.5 and 160.9 seconds 0.04 cc. of oxygen was absorbed by the impurity and 2.06 cc. by the hexaphenylethane. As this proviso will not hold near the end of the reaction, the approximate method cannot be extended over as great a range as the other. This can be seen by comparing Curves A and B of Fig. 1.

The approximate method introduces an uncertainty of about 10% into a measurement, owing to the fact that it is possible to choose a range of values for the correcting volume which will make the significant measurements correspond to a first-order reaction. This uncertainty increases as the accuracy in the determined volumes of gas decreases. The uncertainties introduced by extrapolation of the side reaction are less.

Owing to the somewhat large errors introduced in the way described above, a great many experiments were performed. All the chief points discussed in the text are based on averages of more than forty individual experiments.

Throughout the rest of the text the rate of change of the logarithm of the concentration of the hexaphenylethane under otherwise constant conditions will be referred to as the rate constant for those conditions, and will be represented by the letter K. The actual values given will be those obtained by the approximate method of correction. The units are reciprocal seconds.

Variation of Rate Constant with Oxygen Pressure.—The results obtained by changing the partial pressure of oxygen but keeping the temperature constant at 0° are shown in Table III.

It will be noticed that K changes considerably with change of the partial pressure of oxygen. Conant and Evans[2] have published measurements of the rate of the reactions of several dixanthyls with oxygen. They have shown that the rate of absorption of oxygen by these substances is inde-

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[2] Conant and Evans, THIS JOURNAL, **51**, 1925 (1929).

TABLE III

VARIATION OF RATE CONSTANT WITH OXYGEN PRESSURE

Partial pressure of oxygen, atm.	No. of observations	Rate constant Av., 1/sec.	Rate constant Av. dev., 1/sec.
0.93	17	0.0124	±0.00071
.80	4	.0118	.00005
.60	4	.0105	.0003
.55	5	.0104	.0003
.43	3	.00989	.0003
.31	3	.00837	.00029
.20	11	.00735	.00017

pendent of the oxygen pressure. This difference in the kinetics of the oxidation of hexaphenylethane and of the related dixanthyl is not surprising as it is accompanied by a thousand-fold change in the rate constants and more than 10,000 calorie change in the heat of activation.

It has been shown in the introduction that hexaphenylethane can absorb oxygen by a reaction whose rate is independent of the oxygen pressure. Consequently there must be a second mechanism for the oxidation of hexaphenylethane.

The alternatives for this mechanism are either a reaction of an undissociated but active form of hexaphenylethane, or a dissociation into an isomer of triphenylmethyl, followed by a combination with oxygen. This second form must, however, be colorless, and it must recombine more rapidly than it reacts with oxygen. This latter alternative agrees with the suggestion of Gomberg and Sullivan[3] that triphenylmethyl exists in two forms, which differ in color. However, the authors favor the first alternative on account of its greater simplicity. The experimental results can be equally well explained, whether the oxygen combines with a colorless free radical or with an active but undissociated form of hexaphenylethane. We shall in future refer to the second mechanism as the direct oxidation.

If the values of K are plotted against the pressure of oxygen the points seem to fall on a curved line. This is shown in Fig. 2, in which Curve A is the best parabola and Curve B is the best straight line.[4]

The equation for the straight line is $K = 0.00628 + 0.00678\, P_{O_2}$. This equation means that there are two independent mechanisms. One of these is independent of the oxygen pressure, and has a rate constant equal to 0.00628 reciprocal seconds. Its rate is that of the dissociation into free radicals. The rate of the other reaction is proportional to the oxygen pressure. Its rate constant is 0.00678 in reciprocal seconds and reciprocal atmospheres.

The equation of the parabola is $K = 0.00511 + 0.01225\, P_{O_2} - 0.004715\, P_{O_2}^2$. The probable percentage error calculated for the coefficient of $P_{O_2}^2$

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[3] Gomberg and Sullivan, THIS JOURNAL, **44**, 1822 (1922).

[4] These curves are the most probable of their respective types, taking all the values given in Table III into consideration, but the circles represent mean values.

is 23.3%. The value of this coefficient is, therefore, more than four times the probable error, which formally means that the curvature is real. However, the calculation of probable error does not take into account any consistent error. Thus although the passage of oxygen across the gas–liquid interface was sufficiently rapid to eliminate any large errors, it is possible that the small curvature of the plot may be due to a slight delay involved in this process. However, having given this warning, we shall treat the curvature as significant.

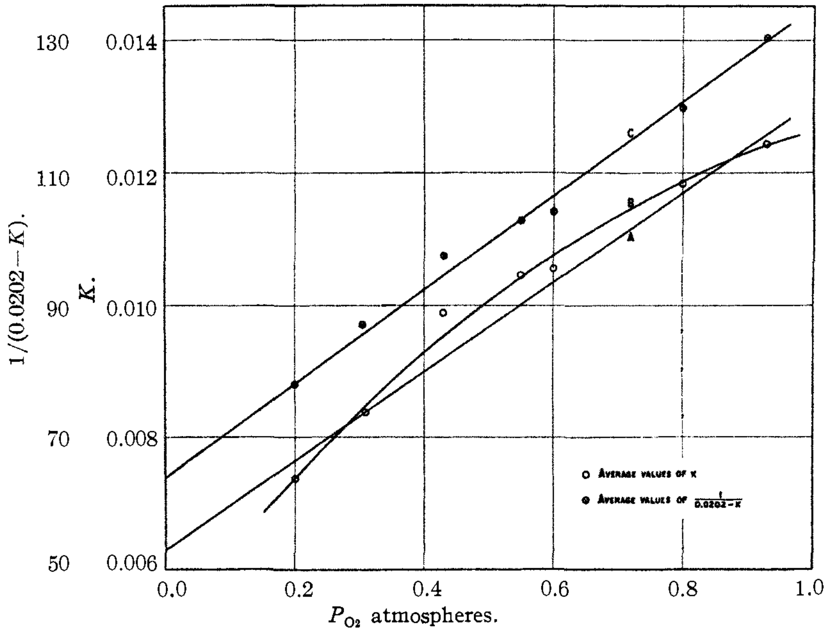

Fig. 2.—Variation of the rate constant with oxygen pressure.

This curvature could be explained by assuming that there are two independent mechanisms. One of which has a rate independent of the oxygen pressure and the other has a rate proportional to a fractional power of the oxygen pressure. The measurements would indicate that this fractional power is the square root. However, it would be necessary to assume an unlikely mechanism in order to account for the proportionality between the reaction rate and the square root of the oxygen pressure.

It is more probable that the direct oxidation is first order with respect to oxygen. The curvature may then be due to the formation of an active intermediate whose rate of return to the normal form is near that of its oxidation. In such a case the intermediate reaches a steady state during the reaction, and its concentration depends, not only on the concentration of hexaphenylethane, but also on the rate of oxidation. If the dissociation depends on the same active intermediate, the steady state depends on the summed effects of the two mechanisms. In both cases the mathematical expression for the kinetics is $K = K_0 - 1/(a + bP_{O_2})$. In the next paragraph we have derived this equation for the more complex case.

Let P_1, P_2 and P_3 represent the specific rate constants of the reactions of active hexaphenylethane to normal hexaphenylethane, of dissociation, and of reacting directly with oxygen, respectively. The probabilities that the life of an individual among these active forms is eventually terminated by each of these processes are, respectively

$$\frac{P_1}{P_1 + P_2 + P_3P_{O_2}} \qquad \frac{P_2}{P_1 + P_2 + P_3P_{O_2}} \qquad \frac{P_3P_{O_2}}{P_1 + P_2 + P_3P_{O_2}}$$

The sum of these probabilities is unity.

$$\frac{P_1}{P_1 + P_2 + P_3P_{O_2}} + \frac{P_2 + P_3P_{O_2}}{P_1 + P_2 + P_3P_{O_2}} = 1$$

If the steady state concentration of the active form is small compared to the concentration of the normal form, the rate of formation of the intermediate is equal to that of its decay. If K_0 is the rate constant for its formation

$$K = K_0\left(\frac{p_2 + p_3P_{O_2}}{p_1 + p_2 + p_3P_{O_2}}\right) = K_0 - \frac{p_1}{p_1 + p_2 + p_3P_{O_2}}K_0$$

Replacing $p_1 + p_2/(p_1K_0)$ and $p_3/(p_1K_0)$ by the constants a and b, respectively, $K = K_0 - 1/(a + bP_{O_2})$.

The constants in this equation can be obtained from the experimental values by a graphical method. The equation is expressed in the form $1/(K_0 - K) = a + bP_{O_2}$. Various values are assumed for K_0, in order to find the range of values for which the quantity $1/(K_0 - K)$ is a linear function of P_{O_2}, within the experimental accuracy of the determinations of K and P_{O_2}. The range of values found was not very great, and the mean value, 0.0202 reciprocal seconds, was chosen for K_0. Curve C in Fig. 2 is this graph. The slope of the line $1/(K_0 - K)$ is b, and its intercept with the ordinate is a. The values found are $a = 64$ seconds and $b = 71$ seconds times reciprocal atmospheres.

The rate of the dissociation reaction is $K_1 - (1/a)$, whether or not the two mechanisms depend on the same intermediate. The value = 0.0046 reciprocal seconds. This compares favorably with 0.0051, the value obtained by extrapolating the parabola to $P_{O_2} = 0$. If the two mechanisms depend on the same intermediate, its rate constant of formation is K_0; but if this substance is only involved in the direct oxidation, the constant is equal to $1/a$.

There are thus three possible theories of the kinetics of the mechanism of the reaction which we have called the direct oxidation. The first is that this reaction is strictly first order with respect to oxygen. The second is that it depends on an intermediate form of hexaphenylethane whose concentration is kept below its equilibrium value. The third is that the substance which is held in a steady state is an intermediate in both the dissociation and direct oxidation. The actual results favor the second and third hypotheses, but these two are not experimentally distinguishable, as they correspond to the same mathematical expression for the variation of K with P_{O_2}.

No matter which theory of the kinetics is correct, a considerable fraction of the reactions occurs through the mechanism of direct oxidation, when oxygen at one atmosphere is used. These fractions may be calculated. They are approximately $^1/_2$, $^3/_4$ and $^5/_6$ on the first, second and third assumptions, respectively.

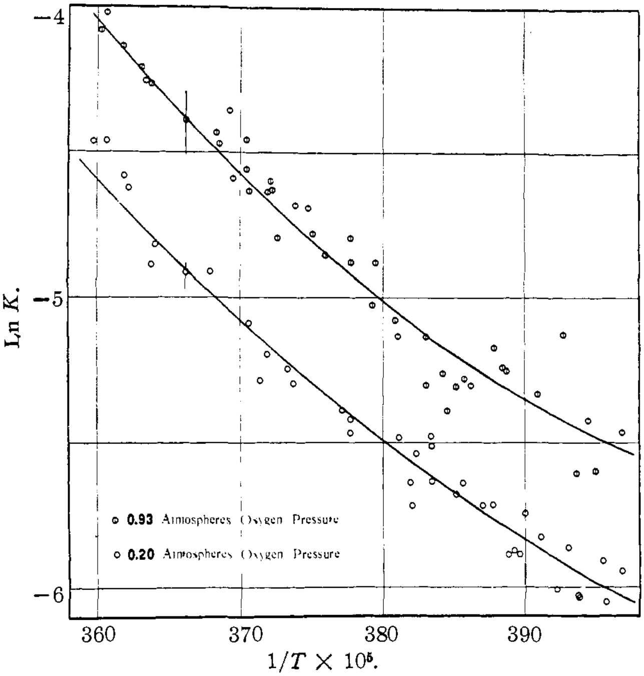

Fig. 3.—Variation of the natural logarithm of the rate constant with the reciprocal of the absolute temperature.

Variation of *K* with Temperature.—The rate constants with 0.93 and 0.20 atmospheres of oxygen were measured from 5 to −21°. A large number of experiments were performed, and the logarithms of the results were plotted against the reciprocal of the temperature. By means of a least square method of reduction of the data the most probable parabolas were calculated. These parabolas and the individual data are shown in Fig. 3. Only the average values of $\ln_e K$ at 0° are shown, as the complete data for K at 0° may be found in Table III. The complete data are given in Tables IV and V.

TABLE IV

RATE CONSTANTS AT 0.93 ATMOSPHERE OF OXYGEN

T	K	T	K	T	K
4.45	0.0169	0.00	0.0122	− 9.35	0.00655
4.25	.0179	.00	.0127	− 9.55	.00759
3.25	.0160	.00	.0133	−10.4	.00622
2.33	.0153	.00	.0112	−10.6	.00589
2.2	.0133	−1.6	.0119	−12.0	.00497
2.05	.0142	−1.7	.0114	−12.0	.00589
1.75	.0141	−2.25	.0128	−12.8	.00519
0.00	.0115	−2.45	.0102	−13.0	.00455
.00	.0111	−3.1	.0116	−13.4	.00496
.00	.0111	−3.1	.0105	−13.85	.00507
.00	.0112	−3.3	.00971	−14.15	.00496
.00	.0132	−4.2	.00969	−15.2	.00566
.00	.0125	−4.35	.01005	−15.6	.00528
.00	.0134	−4.45	.00973	−15.75	.00523
.00	.0119	−4.75	.00825	−17.3	.00482
.00	.0123	−5.6	.00926	−18.35	.00592
.00	.0129	−6.25	.00917	−19.0	.00367
.00	.0126	−6.4	.00839	−19.6	.00440
.00	.0128	−7.1	.00781	−19.85	.00370
.00	.0135	−8.25	.00825	−21.1	.00422
.00	.0137	−8.25	.00759		

TABLE V

RATE CONSTANTS AT 0.20 ATMOSPHERE OF OXYGEN

T	K	T	K	T	K
4.8	0.01152	0.00	0.00743	−13.4	0.00342
4.15	.01155	−1.3	.00736	−13.8	.00355
3.25	.01024	−3.3	.00618	−14.7	.00328
3.0	.00984	−3.85	.00506	−15.15	.00328
2.55	.00957	−4.25	.00554	−15.9	.00277
1.75	.00756	−5.2	.00528	−16.15	.00281
1.55	.00810	−5.5	.00500	−16.45	.00278
0.00	.00736	−7.95	.00457	−16.7	.00320
.00	.00756	−8.35	.00422	−17.45	.00295
.00	.00747	−8.35	.00443	−18.15	.00246
.00	.00696	−10.7	.00416	−18.65	.00285
.00	.00751	−11.25	.00356	−19.1	.00240
.00	.00746	−11.3	.00329	−19.15	.00239
.00	.00751	−11.5	.00387	−20.2	.00272
.00	.00744	−12.25	.00357	−20.4	.00235
.00	.00696	−12.3	.00417	−21.1	.00262
.00	.00724	−12.3	.00404		

The equations for these parabolas are $Y = -0.03415 - 5890X + 4.98 \times 10^6X^2$ for 93% oxygen, and $Y = -0.5851 - 5220X + 3.45 \times 10^6X^2$ for 20% oxygen. In these equations $Y = \ln K + 4$, and $X = 1/T - 0.0036$.

These curves are approximately parallel, almost to within the probable errors. Thus the probable errors in the coefficients of X are 207 and 261, respectively, while the difference between the coefficients is 670. The probable errors in the coefficients of X^2 are 0.569×10^6 and 0.707×10^6, respectively, and the difference between the coefficients is 1.53×10^6. The curvature appears to be real, for in the first equation the coefficient of X^2 is nearly nine times the probable error, and in the second the coefficient of X^2 is nearly five times the probable error. The curve for 93% oxygen was based on sixty-two measurements and that for 20% oxygen on fifty-two. The values of K at 0° calculated from these equations both differ by less than 2% from the average values obtained at this temperature.

The heat of activation of a reaction may be calculated from the rate of change of the logarithm of the velocity constant with the reciprocal of the temperature. The equation is $\partial \log_e K/\partial(1/T) = -E/R$. If such an equation is applied to the reaction of oxygen with hexaphenylethane, the calculated value of the heat of activation will depend on the temperature. Thus with 93% oxygen the apparent heat of activation is 10,500 calories at 0°, 8900 calories at $-6°$ and 4800 calories at $-20°$. With 20% oxygen the heats of activation at these temperatures are 9500, 8400 and 5500 calories, respectively. Since the changes of the heat of activation with temperature depend on the curvature of the plot of $\log K$ against $1/T$, this dependence of E on the temperature is presumably real.

Such a variation of the value of $\partial \log K/\partial(1/T)$ with the temperature could be explained by the double mechanism of the reaction; but this would necessitate that the dissociation and direct oxidation have very different heats of activation. In this case the values of $\partial \log K/\partial(1/T)$ would change markedly when the percentage of oxygen is varied, but the differences between the values for 93 and 20% of oxygen are only slightly in excess of the probable errors. One is, therefore, forced to the conclusion that this anomalous change of $\partial \log K/\partial(1/T)$ with the temperature has nothing to do with the double mechanism of the reaction, but is a characteristic of both the dissociation and the direct oxidation, or that the result is due to some consistent experimental error. Of course, this is not the first time that the logarithm of a reaction rate has been found not to be a linear function of the reciprocal of the temperature.

It is not strictly correct on the activation theory of reactions to use the same equation for calculating the change of K with the temperature for both the dissociation and direct oxidation, for the latter is a bimolecular reaction. The proper equation for second-order rate constants is $\frac{\partial(\ln K - \frac{1}{2}\ln T)}{\partial(1/T)} = -\frac{E}{R}$, but the value of $\frac{1}{2}\frac{\partial \ln T}{\partial(1/T)}$ is smaller than the prabable errors. Also the variation of the rate of the direct oxidation with temperature is dependent on the rate of change of solubility of oxygen in carbon tetrachloride with temperature. This effect is also negligible.

It may be noted that the parallelism of the curves obtained with 93 and 20% of oxygen shows that the heats of activation of the dissociation and direct oxidation have nearly the same magnitudes.[5] This would suggest that little or no energy is needed to activate the oxygen. This to some extent confirms the view of G. N. Lewis that the electronic structure of oxygen is $:\overset{\cdot}{\underset{\cdot\cdot}{O}}:\overset{\cdot}{\underset{\cdot\cdot}{O}}:$, and as such does not require activation in order to react.

The Effect of Inhibitors.—Bäckström[6] has found that the absorption of oxygen by benzaldehyde in the dark is slowed down to a great extent by many substances. Diphenylamine, anthracene and phenol are notable examples of these inhibitors. The effects of these substances were tried. The inhibitors were used in concentrations of 0.005 molal, which is about one-fifth of the concentration of the hexaphenylethane. The two substances did not mix until the experiments were started by the breaking of the container for the hexaphenylethane. The experiments were carried out at 0° and at an oxygen pressure of 0.20 atmosphere. The diphenylamine and anthracene had no appreciable effect; with the former substance $K = 0.00693$ reciprocal seconds was the average of two experiments, and with the latter 0.00725 reciprocal seconds was the average of two experiments. The mean value of K obtained with pure carbon tetrachloride was 0.00735 reciprocal seconds. The value $K = 0.00693$ in the presence of diphenylamine is perhaps a little lower than what might be expected on pure chance; but in this case the diphenylamine was attacked, and much color developed in the solution. The absorption of any oxygen by the diphenylamine would tend to lower K on account of the approximate character of the method used to estimate the total volume of oxygen absorbed by the hexaphenylethane. For this reason it is best to consider the difference between 0.00735 and 0.00693 as experimental error.

With phenol an appreciable increase in the rate was observed. The average of two measurements was $K = 0.0110$ reciprocal seconds. This is more than a 50% increase in the rate, which is much greater than the probable experimental error.

Summary

Measurements were made on the rate of oxygen pressure by carbon tetrachloride solutions of hexaphenylethane under the conditions of constant temperature, of constant oxygen pressure and of vigorous shaking.

The experiments were carried out at many temperatures from 5 to −21°, and with several partial pressures of oxygen from 0.93 to 0.20 atmosphere.

The reaction rate was found to be proportional to the concentration of hexaphenylethane, and to a somewhat complicated function of the oxygen

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[5] Calculations which separate the two heats of activation greatly enhance the experimental error, so that "nearly" may be taken as equivalent to "within 3000 calories."

[6] Bäckström, THIS JOURNAL, **49**, 1460 (1927).

pressure. This function could be best expressed as $K_0 - 1/(a + bP_{O_2})$, in which K_0, a and b are constants.

The character of this function was explained on the assumption that there are two mechanisms, for the reaction. One of these is a dissociation into free radicals followed by a very rapid oxidation. The other is a direct oxidation. On these assumptions alone the function would be $a + bP_{O_2}$; its more complicated form was assumed to be due either to a consistent error, or to the formation of an active intermediate which is held in a steady state other than its true equilibrium ratio with normal hexaphenylethane.

The logarithm of the rate constant was found not to be a linear function of $1/T$. The calculated heats of activation increase with temperature, but are approximately constant to change of the oxygen pressure.

The reaction was not inhibited by diphenylamine, anthracene nor phenol. The last substance increased the rate.

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THE RATE OF REACTION OF CERTAIN ALCOHOLS WITH PARA-NITROBENZOYL CHLORIDE IN ANHYDROUS ETHER SOLUTION

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The speed of ester formation from alcohols and *p*-nitrobenzoyl chloride, in ether solution, has been studied in this Laboratory as a means for measuring the relative reactivity of the hydroxyl hydrogen of the alcohols. In two earlier papers,[2] the influence of the structure of the alcohols on the rate of the reaction has been discussed.

Although the net result of the reaction consists in the formation of a molecule of hydrogen chloride and one of an ester, from one molecule each of alcohol and acid chloride, the second-order velocity constants decrease steadily as the reaction proceeds. This peculiarity was observed with all of the twenty-nine alcohols studied, and it is not dependent on the type of alcohol, whether primary, secondary or tertiary. Furthermore, if the original molal solutions are replaced by half-molal ones, the second-order constants are much smaller and, as before, decrease with the progress of the reaction. If the drop in the value of the second-order reaction constants were attributable to the non-ideality of solution alone,

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[2] (a) Norris and Ashdown, This Journal, **47**, 837 (1925); (b) Norris and Cortese, *ibid.*, **49**, 2640 (1927).