

A TEST OF THE RADIATION HYPOTHESIS
OF CHEMICAL REACTION

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A TEST OF THE RADIATION HYPOTHESIS OF CHEMICAL REACTION.

The viewpoint that thermal unimolecular reactions are to be considered as photochemical reactions with the activating frequencies lying in the infra-red region should be susceptible of experimental test by subjecting a system to radiation from an outside source, and determining whether or not the thermal reaction rate is thereby increased. The difficulties in such an experiment arise from two sources. First, there is the necessity of obtaining a high intensity of infra-red radiation, without at the same time raising the temperature of the reacting substance to such a point that the normal thermal rate is the preponderating effect. In the second place, the extreme opacity of almost all substances to all but the shortest of infra-red rays makes it difficult to find a window that will permit a high intensity over the wide range of frequencies which may be important in activating the molecules. For, since we do not know in what part of the infra-red spectrum the activating frequencies might lie, a conclusive test of the hypothesis should involve the use of all frequencies which are present to an appreciable extent in a hohlraum at the thermal reacting temperature.

Daniels¹ has shown that over a considerable range of frequencies the unimolecular rate of decomposition of N_2O_5 is not appreciably affected by radiation. In the present experiments the effect of infra-red radiation on the rate of racemization of d-pinene in the

liquid state was studied. This reaction has been shown by Smith² to be unimolecular in the gas phase, in the liquid, and in solution in various organic solvents. During the progress of the work Lewis and Mayer³ and Mayer⁴ published the results of a research also dealing with the activation of pinene by infra-red radiation. The conditions of their experiment were such that the molecules in the form of a molecular ray were subjected to an intense field of radiation for a very short length of time. Their method had the advantage of doing away with the necessity of any window and of eliminating collisions so that any effect noticed would be due to radiation. No racemization was detected.

It is to be observed, however, that in experiments in which the reacting substance is at a temperature much below that at which the thermal rate is appreciable, practically all the molecules are in energy states which are very low compared to that of the energy of activation. Hence, since the energy per quantum of infra-red radiation is also small, only a few molecules will be in states from which they can become activated by absorption of a quantum, and thus the increase in rate brought about by the radiation may be unobservably small. This point will be considered in more detail later. For this reason the present experiments are of interest, since they differ from the work of Lewis and Mayer in that pinene was subjected to radiation while at a temperature at which the thermal reaction was just appreciable. The density of radiation in the shorter infra-red has been increased by a large factor over that which prevails in a hohlraum at

the reacting temperature of pinene. Thus if radiation of the frequencies over which it was possible thus to increase the density were active, a large increase in the already measurable rate should have been observed. This was not found, and within the limits of error no increase in rate was observed.

APPARATUS

A considerable amount of experimenting in design of apparatus was carried out to find a method of getting around the difficulties mentioned in the first paragraph. The final form of apparatus, although not completely satisfactory, at least was capable of giving considerable information as to the effect of wave-lengths shorter than 3μ . The liquid temperature was controlled by working in the neighborhood of the boiling point. The transmitting windows were made of thin sheets of mica, which has quite high transmission out to 8μ . The use of a small cylindrical furnace as a source of radiation reduced the ever-present geometrical factor to a considerable extent.

Figure 1 shows the experimental set-up.

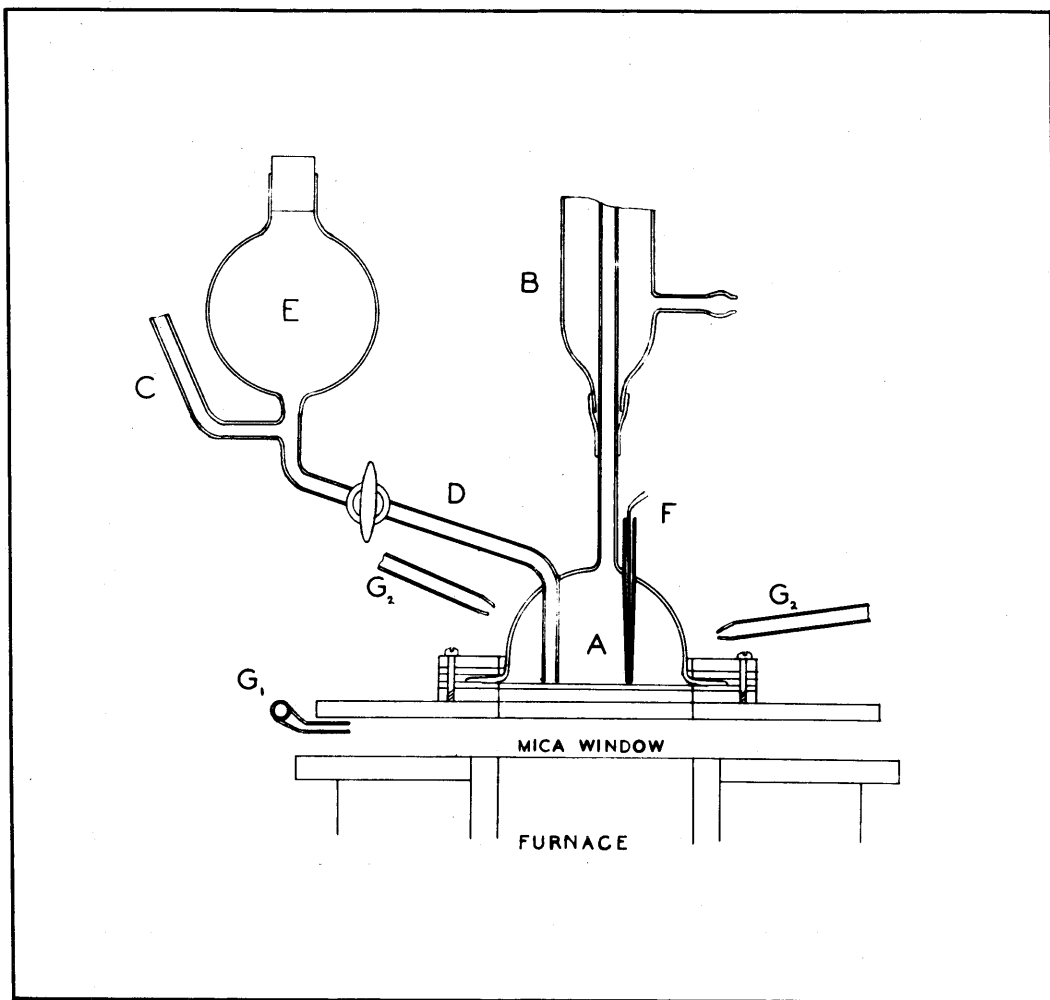


FIG. 1.

The reaction vessel A consisted essentially of a hemispherical glass vessel, 5 cm. in diameter, for which a large window of biotite mica formed the base. Some difficulty was experienced in making the mica-to-glass joint and various cements were tried, none of which would stand the combination of high temperature and solvent action. The glass rim was finally flared out to a brim of about 1/4" and ground flat, the mica sheet 0.04 mm. thick being clamped in place between two brass rings which were held together by screws, thin gas-kets of cork being inserted between the mica and the ground surface, and between the glass and the upper brass ring. The cork was found to have no effect on pinene over a considerable period of operation.

It was found necessary to conduct the experiments in an atmosphere of nitrogen, since considerable oxidation of the pinene was found to take place in the presence of air during the length of time and at the temperature necessary for the runs, and the construction of the reaction vessel made evacuation impossible. The reaction vessel was accordingly connected thru the upright condenser B with a 5-liter bottle filled with dry nitrogen, and arrangements also made to bubble N_2 thru the liquid from the side-tube C. A tube D leading to within a few millimeters of the mica window and connected to a small reservoir E rendered filling and emptying the vessel an easy matter. The small reflux condenser B prevented the loss of pinene during the run.

A thermo-couple F was admitted thru a glass tube to a point within 2-3 mm. of the window, a drop of mercury in the bottom of the

tube giving good thermal contact with the junction. This thermocouple as well as that used in the furnace consisted of a chromel-alumel couple, no. 30 wire, and was used in conjunction with a Leeds and Northrup Potentiometer Indicator. The wire of which the thermocouples were made had been calibrated over the ranges desired, and the thermocouple used in the reaction vessel was checked at the boiling points of water and p-nitrotoluene (237°C). The indicator was compared with a standard potentiometer set-up in use in this laboratory and a plot was then made of temperature against scale reading of the potentiometer indicator in millivolts for the two ranges of indicator scale. The lower scale covered temperatures from 0° to 400° and the upper from 400° to 900° C. Temperatures could be read to within 1° in the liquid and within 2 or 3 degrees in the furnace.

The radiator consisted of a cylindrical alundum tube 5 cm. inside diameter and 25 cm. long, closed at the bottom end, and wound with chromel wire no. 22 in the following manner:- The tube was first completely wound in a spiral groove provided. The whole winding was then covered with a layer of "insalute" cement, and the winding continued back over the upper half of the tube, giving a total length of about 65 ft. of wire. This allowed the upper end of the tube, which was left open, to attain more nearly the temperature of the lower end which was closed and had better heat insulation. The lower end was closed by a disk of asbestos board, on the inside of which was attached a small helical coil containing about 6 ft. of no. 22 chromel wire.

This was covered with a layer of "insalute" which then formed part of the inner wall of the furnace. The whole furnace was packed in asbestos leaving the top open, except that this end was covered by a mica window 0.025 mm. thick to minimize cooling. The thermo-couple junction was imbedded in the wall of the furnace at approximately half way along the tube. The interior walls of the furnace were coated with a mixture of powdered copper oxide with a small amount of "insalute" as a binder, thus giving a surface of a high degree of "blackness".⁵ The furnace was operated at approximately 115 volts, A.C. and 2.2 amperes, the current being adjustable by hand in the body winding and in the end helix separately.

The reaction was followed by observing the optical rotation of the liquid. For this purpose a Lippich polariscope reading to 0.01° was used. The source of illumination was a mercury arc in glass, and the light rendered monochromatic by two filters which absorbed practically everything except the green line $\lambda = 5461 \text{ \AA}$. A 10-cm. tube was used for convenience in handling small quantities of liquid. It had a capacity of about 12 cc. and was enclosed in a water-jacket through which water at 25° C was pumped from a thermostat during measurements.

Pinene: - The pinene used was from Kahlbaum, had an initial rotation at 25° (10-cm. tube) of $+45.3^\circ$, and was slightly yellowish in color. This was distilled under reduced pressure, the middle fraction being taken, which gave a colorless liquid of rotation $+46.2^\circ$ to $+46.6^\circ$, and density_{4⁰}^{25⁰} of 0.857 to 0.855. Gildemeister and Hoffmann⁶ record for d- α -pinene from Grecian turpentine $d_{40}^{25^\circ} = 0.854$.

During early experiments it was noted that pinene which had been subjected to radiation and had been kept at a temperature of 100-150° for an hour or more with air in the vessel showed a considerable increase in rotation, amounting in one case to 0.74° in two hours at 93°. At the same time the liquid had turned quite yellow, due probably to the formation of resin. A change of the same order of magnitude was observed on heating the pinene in a flask for a corresponding time in the presence of air. It was considered likely that oxidation was the cause of this, and accordingly it seemed advisable to try the effect of heating in an atmosphere of nitrogen. It was found that the formation of the yellow substance was almost entirely eliminated, but on heating a sample of freshly distilled pinene the rotation increased to a moderate degree after a short length of time, after which further heating produced no further increase in rotation and only very slight coloration. The reason for this peculiar behavior is obscure but a possible explanation is that a small part of the pinene changed over to some compound of higher rotation, probably limonene. Smith² found some evidence for this in his work. It was therefore necessary to heat the freshly distilled pinene to constant rotation in nitrogen before using it in the reaction vessel and then to carry on the radiation experiments in an atmosphere of nitrogen, under which conditions no such increase of rotation was subsequently observed.

The thermal rate of racemization of a sample of pinene was observed in the gas phase by a method similar to that used by Smith.² The temperature was that of boiling paranitrotoluene (237°C) and the

values of K , obtained were 3.03×10^{-3} and $2.91 \times 10^{-3} \text{ min}^{-1}$ being in good agreement with Smith's value of $3.07 \times 10^{-3} \text{ min}^{-1}$.

Experiments: - About 20 cc. of pinene was placed in the reaction vessel forming a layer over the mica window 1.2 - 1.4 cm. thick. A stream of dried N_2 was then bubbled through the liquid through the tube C for about 10 minutes to displace all the air in the vessel. The stopcock was then closed and the system connected to the N_2 reservoir. The furnace was moved up into a position with the open end 1.7 cm. from the reaction vessel window. A blast of air was passed between the two windows from the fan-shaped tube G, and two jets of air G_2 directed on the upper side of the reaction vessel for the purpose of regulating the temperature of the liquid. The temperature was allowed to rise to the neighborhood of the boiling-point. The liquid was not allowed to boil vigorously in case sudden increase in pressure might rupture the window. Runs were carried on for from 4 to 8 hours, the temperature of the liquid, and that of the furnace, being taken at frequent intervals. The current to the furnace was kept about 2.2 amperes by a hand-operated rheostat. The liquid varied in temperature 4° - 6° during a run and the furnace temperature 10° - 15° . At the expiration of a run the furnace was removed, and the liquid cooled to room temperature by the air blast. It was then expelled into the reservoir E and removed from there to the polariscope tube.

The results of four experiments are shown in Table I. The fifth and sixth columns give the average of a number of polariscope readings, taken before and after the run respectively, individual

readings being reproducible to 0.03° . The seventh column shows the difference, and it is to be noted that a slight decrease was observed in all four runs but that only in the last two does this become greater than the error of measurement. That this decrease is due to the thermal reaction taking place at the temperature of the liquid is shown by the figures of column nine which are calculated values of the decrease for the thermal reaction at the average temperatures given. The constants at these temperatures, which are shown in column eight, were obtained by determining the rate at the boiling point, 156° , and then extrapolating using Smith's value of the heat of activation, $43,710$ cal/mol. The rate at the boiling-point was determined experimentally by keeping pinene at 156° in an atmosphere of nitrogen for periods of 24 hours. The rate thus found, $k_1 = 1.90 \times 10^{-6} \text{ min}^{-1}$, was about 50% higher than that obtained by extrapolating Smith's² data using his rate at 184.6°C .

TABLE I

Run	Furnace temp.	Liquid temp.	Time (min)	α_1	α_2	$\Delta\alpha$	$K_1 \times 10^6$ (min^{-1})	$\Delta\alpha$ (calc)
1	792-823°	143°	260	+46.74°	+46.73°	-0.01°	0.383	-0.01°
3	837-844°	152°	245	+46.71°	+46.70°	-0.01°	1.17	-0.03°
4	846-857°	154°	318	+46.70°	+46.65°	-0.05°	1.50	-0.04°
5	844-858°	150°	500	+46.64°	+46.60°	-0.04°	0.918	-0.04°

Determination of Effective Temperature of Furnace: - In order to determine the intensity of the radiation available for activation it was first necessary to obtain a check on the effective black-body temperature of the furnace. This was done in the following way.

The flux of radiant energy coming from the furnace was determined after the method of Daniels¹ by absorbing the energy in a solution of copper chloride and measuring the rise in temperature produced. Coblenz⁷ has shown that a 2-cm. layer of 2.5% CuCl_2 solution will absorb practically all the energy in the spectral region lying at longer wave-lengths than 0.6μ . Accordingly the furnace was set in position as for a run and a stream of CuCl_2 solution was passed through the reaction vessel at a known rate, the temperature of the stream being taken at points on either side of the reaction vessel. Heating by conduction was reduced by passing a strong blast of air between the furnace and the window to such an extent that the average temperature of the air blast was maintained nearly the same as the temperature of the solution. Thus in one experiment the solution rose from 27.6° to 36.7°C while the average temperature of the air blast was 38.2° and the time of flow for 500 cc. was 518sec. giving a flux of 527 cal. per minute. The average of eight such experiments was 535 cal. per min. with a maximum deviation of 28 cal.

In order to determine the distribution of the energy over the various wave-lengths it was necessary to know the black-body temperature of the source. This was estimated by assuming some temperature and calculating from the geometry of the set-up and the transmission losses the

the corresponding flux into the reaction vessel. This was to be compared with the experimentally determined value, and the assumed temperature corrected to give the correct flux. Thus the flux of radiation through a circular surface of diameter D from a circular black-body surface of the same diameter and parallel to the first at a distance d is given by⁸

$$F_\nu = \frac{1}{2D^2} c u_\nu T_\nu \left(\frac{D^2}{2} + d^2 - d\sqrt{D^2 + d^2} \right) \quad (1)$$

where $F_\nu d\nu$ is the energy per unit area per second in the frequency range ν to $\nu + d\nu$; $u_\nu d\nu$ the density of radiant energy in the same frequency range, corresponding to the black-body temperature of the source; and c the velocity of light. T_ν is the fractional transmission of the intervening windows at the frequency ν .

The total flux may be obtained by integrating the above expression over all values of ν and this was done graphically as follows. The values of u_ν were obtained from Planck's equation

$$u_\nu = \frac{8\pi h \nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{kT}} - 1} \quad (2)$$

and are given in Table II, column 3 for a temperature of 800°C and for frequencies corresponding to wave-lengths from 1 to 9 μ . Values of T_ν were obtained from Coblenz's⁹ data on the transmission of mica, and were corrected for the difference in thickness used here from that used by Coblenz. These are shown in Table II, column 4, and are not carried past 9 μ since beyond that wave-length mica is nearly totally opaque to infra-red. Column 5 gives $u_\nu T_\nu$ and these values are plotted against ν in Figure II. The area under the curve was found to be

1.408×10^{-10} calories per cc.

Substituting in equation (1), $D = 5$ cm., $c = 3 \times 10^{10}$ cm/sec, $d = 2.2$ cm., one obtains

$$F_\nu d\nu = 3.19 \times 10^9 u_\nu T_\nu d\nu \text{ per sq.cm. per second} \quad (3)$$

$$F_{\text{total}} = \pi R^2/4 \times 3.19 \times 10^9 \times 60 \int_0^\infty u_\nu T_\nu d\nu \\ = 529 \text{ cal. per min.}$$

Since the observed value was 535 cal. per min. it seems fair to treat the furnace as a black-body emitting at 800°C , especially as the actual temperature in the middle of the furnace was always $40\text{--}50^\circ$ above this.

FIG. 2.

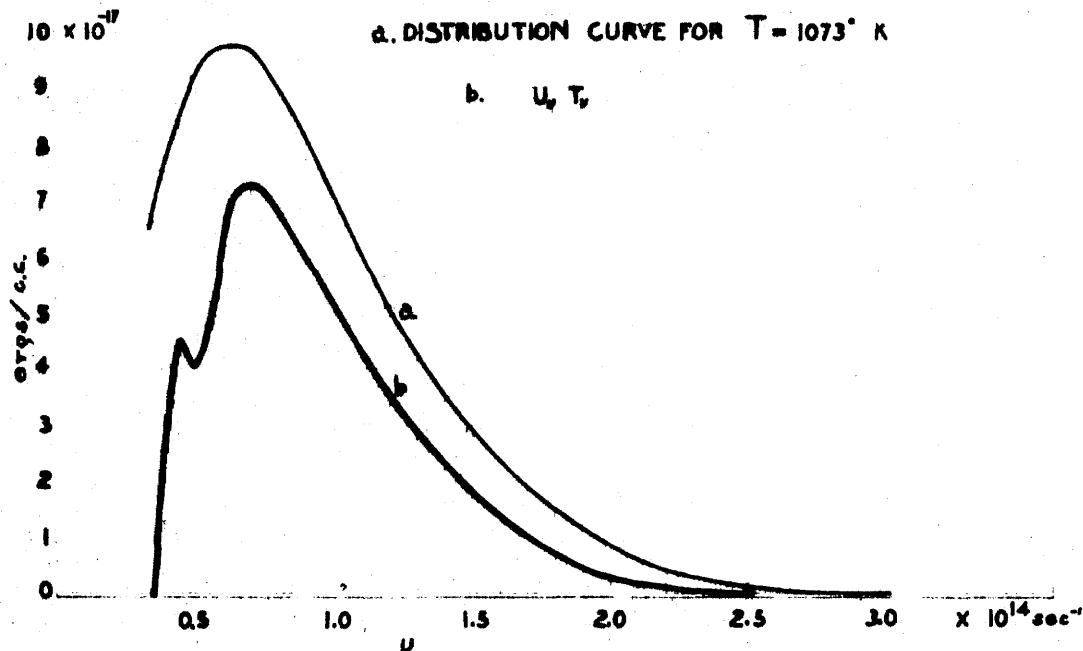


TABLE II

$\lambda (\mu)$	$\mu \times 10^{-14}$	$\mu_p \times 10^{17}$ (800°C)	% Trans. mica	$\mu_p T_p \times 10^{17}$	α (mm ⁻¹)	\bar{I}/I_0	$\bar{\mu}_p \times 10^{19}$	$\mu_p \times 10^{19}$ (152°C)
1	3	0.0255	7.56	0.0019	1.57	0.0455	7.4×10^{-4}	3.69×10^{-9}
1.2	2.5	0.0943	11.1	0.015	1.02	0.0700	8.98×10^{-3}	3.84×10^{-7}
1.5	2	0.819	30.2	0.247	1.02	0.0700	0.148	8.09×10^{-5}
2.0	1.5	2.87	64.0	1.835	1.39	0.0514	0.805	9.85×10^{-3}
2.5	1.2	5.01	71.6	3.59	2.14	0.0334	1.027	0.142
3	1	7.13	72.2	5.16	6.93	0.01031	0.456	0.803
3.5	0.858	8.79	73.9	6.50	18.46	0.0039	0.217	2.49
4	0.75	9.43	75.7	7.14	5.24	0.01363	0.833	5.48
5	0.6	9.75	65.6	6.40	3.30	0.02165	1.19	15.5
5.5	0.546	9.61	49.0	4.71	3.93	0.01817	0.733	21.6
6	0.5	9.21	43.6	4.01				
7	0.429	8.41	53.2	4.48				
8	0.373	7.43	32.5	2.41				
9	0.333	6.63	0.09	0.006				

Intensity of Radiation .- In order to determine whether or not the radiation was of such an intensity that an observable change of rotation would have been noticed had the radiation been effective, we must compare the density of radiant energy which has been produced in the reacting substance with that in a hohlraum at the temperature of the liquid during the irradiation.

The average intensity of radiation in the liquid layer as a fraction of the incident intensity can be obtained from the formula

$$\frac{\bar{I}}{I_0} = \frac{1}{\alpha x_1} (1 - e^{-\alpha x_1})$$

where α is the absorption coefficient and x , the thickness of absorbing material.

Taking Coblenz's¹⁰ data on pinene and absorption coefficients α have been calculated at intervals over the range 1 - 9 μ and are shown in Table II, column 6. The total thickness of the liquid layer was 14 mm. The absorption coefficients vary from 1 to 18 so that the maximum value of $e^{-\alpha x_1}$ is e^{-14} , which is very small compared with 1.

Hence for this thickness
$$\frac{\bar{I}}{I_0} = \frac{1}{\alpha x_1}$$

Values of \bar{I}/I_0 have been calculated over the range of wave-lengths required and are shown in Table II, column 7.

The flux of energy through the lower surface of the liquid is given by equation (3)

$$F_p = 3.19 \times 10^9 \mu_p T_p \text{ per sq.cm.}$$

The flux through a boundary at the upper surface of the liquid without considering absorption by the liquid similarly comes out to be

$$F'_\nu = 1.95 \times 10^9 \mu_\nu T_\nu$$

So that the error will be small if we take the average flux as

$$\bar{F}_\nu = 2.57 \times 10^9 \mu_\nu T_\nu$$

And the average radiation density of the frequency ν as

$$\mu_\nu = 2.57 \times 10^9 \frac{\mu_\nu T_\nu}{c} \frac{\bar{I}}{I_0} = 0.0857 \mu_\nu T_\nu \frac{\bar{I}}{I_0}$$

Column 8 of Table II shows the calculated values of $\bar{\mu}_\nu$ and column 9 the values of μ_ν at 152°C corresponding to the temperature of the liquid.

Figure 3 shows a plot of $\bar{\mu}_\nu$ and μ_ν ($t = 152^\circ$) against frequency ν . It is to be noticed that out to a wave-length of nearly 3μ the density of radiation produced is very much greater than that at 152° so that if these shorter wave-lengths were active the reaction rate should have been increased many times. Past 3μ the induced density falls considerably below the other so that these experiments do not furnish any information as to the effect of these longer wave-lengths. The intensity at the red end of the visible was also relatively high, and it is here we would expect an effect on the basis of the simple radiation hypothesis, since for pinene the total energy of activation corresponds to a wave-length of 0.65μ .

1.0×10^{10}

ergs/cm^2

0.5

0 $\nu \rightarrow$ 0.5 1.0 1.5 2.0 2.5 3.0 $\times 10^{14} \text{ sec}^{-1}$

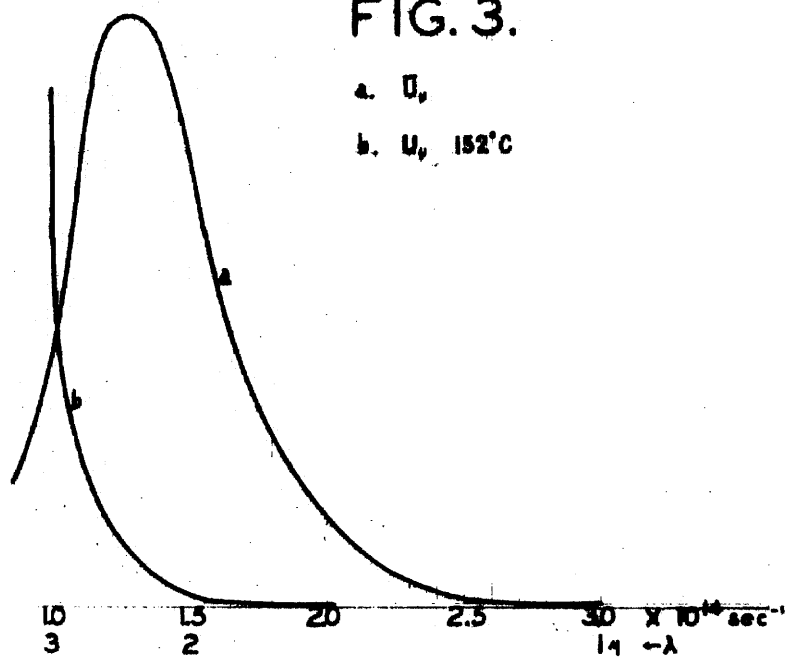
5 4 3 2 1

$\lambda \rightarrow$

FIG. 3.

a. U_v

b. U_v , 152°C



DISCUSSION

The results obtained here show that radiation in the infrared out to wave-lengths of 3μ does not accelerate the rate of racemization of pinene, and therefore that in this thermal reaction radiation over this range is not the agency which keeps up the quota of activated molecules. One must still admit the possibility, however, of longer wave-lengths being active, since at a temperature of 152°C the maximum intensity of black-body radiation lies out as far as 12.5μ . Further, both N_2O_5 and pinene have strong absorption bands in the region beyond 3μ .^{10,11}

Turning to the work of Lewis and Mayer, it appears at first sight as though they had extended the range of wave-lengths over which radiation is shown to be inactive in this reaction out to 13μ . The method of treatment used by them, however, seems to require some further analysis. Under the conditions of the experiment pinene coming from a nozzle at a temperature of 93°C was shot through a radiation field corresponding to a black-body temperature of about 1000°K and was condensed out on the farther side by liquid air. The length of time during which the molecules were exposed to the radiation was calculated to be 1.2×10^{-4} sec. To treat this data by the method which has been applied to the experiments just described, one must first ask the following question. By what factor is it necessary to increase the thermal reaction rate at 93° in order that it may be observable during the time of exposure? Mayer has calculated that the minimum rate which

he could have observed is $k = 431 \text{ sec}^{-1}$, which would be the thermal rate at 800°K . By using the value here given of the reaction rate at 156°C and extrapolating in the usual manner, one finds the thermal rate at 93°C to be $4.68 \times 10^{-12} \text{ sec}^{-1}$. Hence the rate at 93° must be increased by a factor of 10^{14} if it is to be observable. This can take place in two ways, assuming that radiation is to be the activating agency. First, the density of radiation over the frequencies to be tested may be increased by a factor of 10^{14} over the corresponding densities in a hohlraum at 93°C . Second, the molecules by successive absorption of quanta may be brought up to such a distribution of internal energies as would prevail at 800° , the thermal reaction then taking place. Let us now examine these processes in detail.

The frequency at which the radiation density at 1053°K , the temperature of the furnace, is just 10^{14} times as great as the corresponding density at 93° (366°K) may easily be found from the Wien law, which is applicable in the region considered, and gives us the expression

$$\frac{\mu_\nu}{\mu_{\nu'}} = \frac{e^{\frac{h\nu}{kT'}}}{e^{\frac{h\nu}{kT}}} \quad \text{where} \quad \frac{\mu_\nu}{\mu_{\nu'}} = 10^{14} \quad \text{and} \quad \begin{array}{l} T = 1053^\circ\text{K} \\ T' = 366^\circ\text{K} \end{array}$$

This gives for ν the value $3.79 \times 10^{14} \text{ sec}^{-1}$ corresponding to a wave-length of 0.79μ . At shorter wave-lengths the density produced by the furnace is greater than 10^{14} times the density at 93° and at longer wave-lengths it is less. (The fact that the actual distribution of energy in the furnace as used by Mayer was such as to produce densities

at these frequencies two or three times that of black-body radiation at 1053°K makes only a very slight change in this result.) Therefore if we regard the molecules as remaining throughout the length of furnace substantially in the state which they have at 93°C, then radiation has been proved to be inactive in this experiment only for wave-lengths shorter than 0.79 μ .

Now let us consider the second possibility that by successive absorption of quanta the molecules are distributed in states corresponding to a considerably higher temperature than 93°C throughout a considerable portion of the length of the furnace, as Mayer assumed to be the case. Since no collisions were taking place the conditions were extremely favorable to such a possibility, provided that the time of exposure was long enough. But this does not appear to be the case, since if radiation of relatively low frequency is to be active, it is evident that most of the molecules will have to make quite a number of quantum jumps before the new condition corresponding say to 800° K is reached. However, the average number of quantum jumps made by a molecule per second is equal to $B_{ij} u_{\nu_{ij}}$, where B_{ij} is Einstein's coefficient of absorption and $u_{\nu_{ij}}$ the radiation density of the frequency necessary to transfer the molecule from state i to state j . From correspondence principle considerations¹² a maximum value of B_{ij} can be given as of the order 10^{20} e.g.s. units.* Taking now the maximum intensity in the black-body

*Undoubtedly some arbitrariness is introduced by the use of the value 10^{20} for B_{ij} . This has been set as a probable upper limit and actually for absorption in the infra-red values of 10^{14} to 10^{19} have been found.¹³

spectrum at 1073°K we have

$$\mu_{ij} = 9.75 \times 10^{-17} \text{ ergs-sec. per cc.}$$

and the number of jumps per second is about 10^4 . Thus in 1.2×10^{-4} seconds a molecule will not make more than one jump on the average. If this be so, then the distribution of molecules among the energy states will not be very different from that prevailing at 93°, and hence the case will be practically that first considered. This means that, although the molecules were subjected to a radiation field of high intensity, the time of exposure was so short that it is not likely that the molecules could absorb frequently enough to vary appreciably their internal energies from those prevailing at 93°C. The average energy would be somewhat increased it is true, but so little that the limit of effective wave-lengths would certainly not be as far out as 13μ and it is doubtful if it would be much below 1μ .

Hence Mayer's experiment has not proved the ineffectiveness of radiation out to 13μ in the thermal racemization of pinene, but has only shown that in the short length of time during which the molecules remained in his furnace, radiation corresponding approximately to 1053°K was not able to raise his molecules from states corresponding to 93°C to states high enough so that the reaction was appreciable.

The foregoing discussion makes evident the desirability, in testing the radiation hypothesis, of working in the presence of excess radiation at temperatures where the thermal rate is already appreciable, as was done in the present experiments.

THE MAXIMUM RATE OF ACTIVATION

In conclusion certain theoretical considerations will now be presented which make it seem in any case extremely unlikely that radiation is the sole activating factor in unimolecular reactions. Let us assume the molecule to be a simple oscillator with one degree of freedom. Between the normal level and the activated state there will presumably be a number of oscillational levels which will get closer together as we approach the activated state. This will be caused by the anharmonic nature of the oscillation, and will correspond to a gradual weakening of the bond until reaction can take place. If the system of molecules is at a definite temperature and reaction is taking place the molecules will be distributed among the intermediate levels fairly closely in accordance with the Maxwell-Boltzmann distribution law, although the distribution may deviate from this in the activated state or states. If now in a given time a certain number of molecules are removed from the activated states by reaction, this number must be replaced by molecules from still lower states, and so on down to the lowest oscillational level. Our postulate is that such replenishing is brought about entirely by the absorption of radiation by the molecules, and we shall now examine this process in detail for a particular one of the above steps.

Since the oscillation is anharmonic the molecule will in general change its quantum number not only by one, but also by larger integers. However, if we confine our attention to a state intermediate

between the lowest and those that are chemically activated it seems reasonable to assume that the major fraction of the molecules which come to this state from below, come from the next lower state. In other words, the deviation from harmonicity has not become very great.

The rate at which a molecule can go from state i to state j by absorption of radiation is given by

$$Z = N_i B_{ij} \mathcal{U}_\nu \quad (1)$$

where N_i is the number of molecules in state i , B_{ij} is Einstein's coefficient of absorption, and \mathcal{U}_ν is the radiation density at the frequency ν such that $\epsilon_j - \epsilon_i = h\nu$

This rate must be compared with the rate of reaction. Presumably the rate given by equation (1) must be very much greater than the reaction rate since we have also deactivational processes taking place.

Hence we may write

$$N_i B_{ij} \mathcal{U}_\nu \gg k_i N \quad (2)$$

where k_i is the specific reaction rate, and N the total number of molecules. For the lower states this inequality is very likely to be true since N_i is a large number, and we shall investigate the case for one of the higher states, still considerably below the state of activation.

Assume that N_i is given by the Maxwell-Boltzmann expression

$$N_i = \frac{N e^{-\frac{\epsilon_i}{KT}}}{\sum_i e^{-\frac{\epsilon_i}{KT}}}$$

We also have, in accordance with the Planck radiation law,

$$\begin{aligned} u_\nu &= \frac{8\pi h \nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{kT}} - 1} \\ &= \frac{8\pi}{h^2 c^3} (\epsilon_j - \epsilon_i)^3 \frac{1}{e^{\frac{\epsilon_j - \epsilon_i}{kT}} - 1} \end{aligned}$$

and by substituting in (2) we obtain

$$\frac{N e^{-\frac{\epsilon_i}{kT}}}{\sum_i e^{-\frac{\epsilon_i}{kT}}} B_{ij} \frac{8\pi}{h^2 c^3} (\epsilon_j - \epsilon_i)^3 \frac{1}{e^{\frac{\epsilon_j - \epsilon_i}{kT}} - 1} > k_1 N \quad (3)$$

If the oscillation is approximately harmonic, we can write $\epsilon_j - \epsilon_i = \epsilon$ and $\epsilon_i = n\epsilon$ where n is an integer, and ϵ is the energy difference between successive levels. This permits us to rewrite the foregoing equation in the form

$$\frac{8\pi B_{ij}}{h^2 c^3} \epsilon^3 \frac{e^{-\frac{n\epsilon}{kT}}}{\sum_n e^{-\frac{n\epsilon}{kT}}} \frac{1}{e^{\frac{\epsilon}{kT}} - 1} > k_1$$

Now

$$\sum_n e^{-\frac{n\epsilon}{kT}} = \frac{1}{1 - e^{-\frac{\epsilon}{kT}}} = \frac{e^{\frac{\epsilon}{kT}}}{e^{\frac{\epsilon}{kT}} - 1}$$

So that we finally obtain

$$\frac{8\pi B_{ij}}{h^2 c^3} \epsilon^3 e^{-\frac{(n+1)\epsilon}{kT}} > k_1 \quad (4)$$

If now we take $(n+1)\epsilon = \frac{2}{3} \epsilon_a$ where ϵ_a is the energy of activation calculated from the temperature coefficient and put $k_1 = K' e^{-\frac{\epsilon_a}{kT}}$

we have

$$\frac{8\pi h B_{ij}}{c^3} \nu^3 e^{-\frac{2}{3} \frac{\epsilon_a}{kT}} > K' e^{-\frac{\epsilon_a}{kT}}$$

or

$$\frac{8\pi h B_{ij}}{c^3} \nu^3 e^{\frac{E_a}{3kT}} > K' \quad (5)$$

To determine the maximum possible rate let us put $B_{ij} = 10^{20}$ and give ν the value it has at the maximum intensity in the spectrum at some reacting temperature. For example, for the decomposition of N_2O_5 , we have $K' = 4.56 \times 10^{13} \text{ }^{(13)}$ and $E_a = 24,700 \text{ cal/mol}$, giving us at $298^\circ K$

$$\frac{E_a}{3kT} = \frac{E_a}{3RT} = \frac{24,700}{3 \times 1.985 \times 298} = 13.9$$

$$\text{and } e^{\frac{E_a}{3kT}} = e^{13.9} = 1.1 \times 10^6$$

Furthermore, we have

$$\nu_{\text{max}} \text{ at } 298^\circ = 1.76 \times 10^{13} \text{ sec}^{-1}$$

$$h = 6.554 \times 10^{-27}$$

$$c^3 = 2.7 \times 10^{31}$$

Substituting, we have for the left-hand side of the inequality

$$\frac{8\pi \times 6.554 \times 10^{-27} \times 10^{20} \times 1.76^3 \times 10^{39} \times 1.1 \times 10^6}{2.7 \times 10^{31}} = 3.34 \times 10^9$$

This is to be compared with 4.56×10^{13} .

Thus we see that the rate at which molecules are transferred from one particular lower state to the next higher is not even as fast as the rate of reaction. This is all that needs to be shown in order to invalidate an hypothesis of total activation by radiation, but it may be noticed that the discrepancy gets larger as we go to higher states. However, as the molecule increases in energy its oscillation becomes more anharmonic and hence the absorption of other frequencies tends to increase the rate of supply to any one level somewhat. It

does not seem that this could counteract the enormous discrepancy between the reaction rate and the rate of maintenance of the quota of partially activated molecules.

In the above treatment we have considered the molecule as a single oscillator, this oscillator corresponding to the bond which was to be broken, and we have seen that the rate at which the molecules are transferred between the higher intermediate states is too small to keep up the reaction rate. Another possibility suggests itself, however, namely that there may be some interaction with the other oscillators present in the molecule in such a way that energy is transferred from them to the particular oscillator of interest, leading to dissociation. Thus it may only be necessary that the total energy of the oscillators be equal to or in excess of the energy of activation, in which case each oscillator would only have to contribute a fraction of the energy required. After the molecule as a whole has acquired the necessary energy, the chance may be very large that this energy will get into the particular oscillator of interest, so that the controlling factor would be the rate at which the molecule as a whole can acquire the energy of activation.

In order to investigate this possibility, let us take the particular case used above, the decomposition of N_2O_5 at 298°K . Let us consider the N_2O_5 molecule as consisting of seven oscillators which for simplicity we will take to have the same frequency. Let this frequency correspond to that of maximum intensity in the black-body spec-

trum at 298°K. That is, $\nu = 1.76 \times 10^{13} \text{sec}^{-1}$. It also seems reasonable to assume that these oscillators remain essentially harmonic even when the total energy of the molecule is equal to the energy of activation.

The number of molecules in the i^{th} quantum state is given by

$$N_i = \frac{N e^{-\frac{\epsilon_i}{KT}}}{\sum_i e^{-\frac{\epsilon_i}{KT}}}$$

where the i^{th} state is defined by assigning definite quantum numbers to each degree of freedom in the molecule. The number of molecules for which the total energy is ϵ_i irrespective of the way in which it is distributed among the various degrees of freedom is greater than this by the factor which determines the number of ways in which the 7 oscillators can be assigned quantum numbers such that the total energy is equal to ϵ_i . This factor is $(n+7-1)!/n! (7-1)!$ where n is the number of quanta of the frequency ν which are necessary to make up the energy ϵ_i .

The rate at which molecules having energy ϵ_i go up to a state j in which the molecule as a whole possesses one more quantum of energy is then given by the expression

$$Z_{ij} = 7 \frac{(n+7-1)!}{n! (7-1)!} \frac{N e^{-\frac{\epsilon_i}{KT}}}{\sum_i e^{-\frac{\epsilon_i}{KT}}} B_{ij} u_\nu \quad (6)$$

where the quantities introduced have the same meaning as before, except that in this case

$$\sum_i e^{-\frac{\epsilon_i}{KT}} = \sum_n \frac{(n+7-1)!}{n! (7-1)!} e^{-\frac{n h \nu}{KT}}$$

The factor 7 is introduced since we now have 7 times as many possibilities for picking up a quantum.

To evaluate n we may write $n h \nu = \epsilon_i$ and let this energy correspond to the state just below the first activated state such that $\epsilon_i + h \nu = \epsilon_a$

$$\text{Then we have } (n+1)h\nu = \epsilon_a$$

$$n + 1 = \frac{\epsilon_a}{h\nu}$$

Substituting numerical values

$$\begin{aligned} n + 1 &= \frac{24,700 \times 4.182 \times 10^7}{6.06 \times 10^{23} \times 6.554 \times 10^{-27} \times 1.76 \times 10^{13}} \\ &= 14.8 \end{aligned}$$

Hence we may take n as 14.

$$\text{and } (n+7-1)! / n! (7-1)! = 20! / 14! 6! = 3.88 \times 10^4$$

Furthermore we have:

$$\begin{aligned} \sum_{n=0}^{\infty} \frac{(n+7-1)!}{n!(7-1)!} e^{-\frac{n h \nu}{kT}} &= 1 + 7e^{-\frac{h\nu}{kT}} + 28e^{-\frac{2h\nu}{kT}} \\ &+ 84e^{-\frac{3h\nu}{kT}} + 210e^{-\frac{4h\nu}{kT}} + 462e^{-\frac{5h\nu}{kT}} + \dots \end{aligned}$$

This series converges fairly rapidly so it is sufficient to take the first six terms. This gives:

$$\sum_{n=0}^{\infty} \frac{(n+7-1)!}{n!(7-1)!} e^{-\frac{n h \nu}{kT}} = 1.538$$

For μ_ν we have by the Planck law:

$$\mu_\nu = \frac{8\pi h \nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{kT}} - 1}$$

$$\text{where } \frac{h\nu}{kT} = \frac{6.554 \times 10^{-27} \times 1.76 \times 10^{13}}{1.372 \times 10^{-16} \times 298} \\ = 2.82$$

$$\text{Whence } e^{\frac{h\nu}{kT}} = 16.8 \text{ and } \frac{1}{e^{\frac{h\nu}{kT}} - 1} = 0.0633$$

Also we have

$$e^{-\frac{h\nu}{kT}} e^{-\frac{\epsilon_i}{kT}} = e^{-\frac{\epsilon_a}{kT}} \\ \text{or } e^{-\frac{\epsilon_i}{kT}} = 16.8 e^{-\frac{\epsilon_a}{kT}}$$

$$c^3 = 2.7 \times 10^{31} \text{ cm}^3 \text{ sec}^{-3}$$

$$B_{ij} = 10^{20} \text{ c.g.s. units}$$

Therefore:

$$Z_{ij} = \frac{8\pi \times 6.544 \times 10^{-27} \times 1.76^3 \times 10^{39} \times 0.0633 \times 10^{20} \times 7 \times 3.88 \times 10^4 \times 16.8}{1.538 \times 2.7 \times 10^{31}} N e^{-\frac{\epsilon_a}{kT}}$$

$$= 6.255 \times 10^8 N e^{-\frac{\epsilon_a}{kT}} \text{ molecules per second.}$$

While the reaction rate is given by:¹³

$$Z_{\text{react}} = 4.56 \times 10^{13} N e^{-\frac{\epsilon_a}{kT}} \text{ molecules per second.}$$

Thus the rate of activation in this case also is too small by a factor of 10^{-5} .

It might appear as if the rate of activation could be considerably larger if smaller quanta were used, since in that case the number of ways of distributing them among the oscillators would be increased. This, however, does not help out the situation since the

denominator $\sum_i e^{-\frac{\epsilon_i}{KT}}$ then becomes large, $e^{-\frac{\epsilon_i}{KT}}$ in the numerator becomes smaller and μ_ω becomes less since we are past the maximum. Thus at $\nu = 1 \times 10^{13} \text{ sec}^{-1}$ the value of Z_{ij} is about the same as that calculated above for $\nu = 1.76 \times 10^{13} \text{ sec}^{-1}$.

Hence we may conclude that it is highly improbable that radiation is the agency which keeps up the supply of activated molecules during the reaction, while if the mechanism is partly radiational and partly collisional, the role which radiation plays appears to be a very minor one. This is in agreement, moreover, with the fact that no experimental evidence of reactions being brought about by absorption in the infra-red has been obtained. On the contrary, where reaction by absorption does take place, such absorption in the visible or ultra-violet, corresponding to a change in the electronic structure of the molecule. The energy of quanta in the infra-red is insufficient for such a process. This indicates a fundamental difference between photochemical reactions and thermal reactions, as pointed out by Daniels,¹⁴ and leaves the alternative that the activational processes in the latter type must be collisional, on which basis several very good hypotheses have recently been advanced.¹⁵

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SUMMARY

1. Experiments are described which show that the rate of racemization of pinene is not accelerated by a large increase in the density of radiation over the range of wave-lengths from 1μ to 3μ .
2. The nature of the experiments does not warrant any conclusion as to the effectiveness of wave-lengths longer than 3μ .
3. The work of Lewis and Mayer on pinene is criticised from the point of view of the justifiability of the conclusions which they drew as to the inactivity of the longer wave-lengths, and it is shown that they have not proved that radiation of wave-lengths much below 1μ is inactive in a chemical reaction.
4. The lack of evidence in favor of a radiation hypothesis of thermal reactions is discussed.
5. A theoretical treatment is given which shows that it is unlikely that the thermal reaction rate could be kept up solely by the agency of radiation.

BIBLIOGRAPHY

1. Daniels, J. Am. Chem. Soc., 48, 607 (1926).
2. Smith, ibid., 49, 43 (1927).
3. Lewis and Mayer, Proc. Nat. Acad. Sci., 13, 8, 623 (1927).
4. Mayer, J. Am. Chem. Soc., 49, 3033 (1927).
5. See Coblentz, "Investigations of Infra-red Spectra", Part VII, p. 119.
Carnegie Institution Publication Number 97, 1908,
6. Gildemeister u. Hoffmann, "Die Ätherischen Öle", Vol. I, p. 305.
Schimmel and Co., Leipzig, 1910.
7. Coblentz, Bull. Bur. Stand., 9, 110 (1913).
8. See J. W. T. Walsh, "Photometry", p. 104.
Constable and Co., London, 1926.
9. Coblentz, "Investigations of Infra-red Spectra", Vol. III, p. 49.
Carnegie Institution Publication Number 65, 1907.
10. Coblentz, ibid.
11. Daniels, J. Am. Chem. Soc., 47, 2856 (1925).
12. See Tolman, "Statistical Mechanics with Applications to Physics
and Chemistry", p. 179.
Chemical Catalog Co., 1927.
13. Tolman, J. Am. Chem. Soc., 47, 1524, (1925).
14. Daniels, Chem. Rev., V, 39 (1928).
15. See, for example, Rice and Ramsperger, J. Am. Chem. Soc., 49, 1617 (1927).