

2. The temperature coefficient of this rate does not appear to be 13, as Bell reported, but, when runs under comparable conditions are made, is about 2. It increases somewhat with the temperature, indicating that more than one reaction is occurring.

3. The mechanism suggested by Bell, impact of permanganate ions on an adsorbed film of benzoyl-*o*-toluidine, does not disagree with the data, but it is impossible to make any but the crudest sort of verification. Other mechanisms are possible.

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A TEST OF THE RADIATION HYPOTHESIS OF CHEMICAL REACTION¹

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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.

Daniels³ 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.

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² This is part of a thesis submitted by William Ure to the Division of Chemistry, California Institute of Technology, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

³ Daniels, *THIS JOURNAL*, **48**, 607 (1926).

This reaction has been shown by Smith⁴ 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 Mayer⁵ and Mayer⁶ 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 for 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 of 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 was 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.

Experimental Determination of the Rates

Apparatus.—The liquid pinene was contained in a vessel having a large window of very thin mica, which is highly transparent to the near infra-red, and was subjected to an intense beam of radiation from the open end of a cylindrical furnace kept at 850° which was situated just below the window. The vessel was cooled by air-blasts and the temperature of the liquid was maintained in the neighborhood of the boiling point, 156°.

The experimental arrangement is shown in Fig. 1. The reaction vessel A was a hemispherical glass vessel 5 cm. in diameter, the rim of which was flared out and ground flat, the mica sheet 0.04 mm. thick being clamped in place between two brass rings and a tight seal ensured by inserting cork gaskets. 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

⁴ Smith, *THIS JOURNAL*, 49, 43 (1927).

⁵ Lewis and Mayer, *Proc. Nat. Acad. Sci.*, 13, 8, 623 (1927).

⁶ Mayer, *THIS JOURNAL*, 49, 3033 (1927).

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 through the upright condenser B with a 5-liter bottle filled with dry nitrogen, and arrangement also made to bubble nitrogen through 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. At F a thermocouple was inserted through a thin glass tube.

The radiator consisted of a cylindrical alundum tube 5 cm. in 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

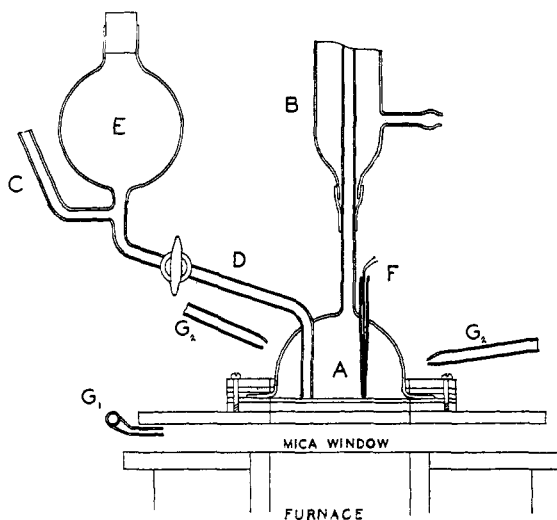


Fig. 1.

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. A thermocouple junction was embedded 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."⁷ 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, using a

⁷ See Coblenz, "Investigations of Infra-red Spectra," *Carnegie Institution Publication Number 97, 1908, Part VII, p. 119.*

polariscope reading to 0.01° . 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° was pumped from a thermostat during measurements.

Material Used.—The pinene was obtained from Kahlbaum. It had an initial rotation at 25° (10-cm. tube) of $+45.3^\circ$ and was slightly yellowish in color. Fractionation under reduced pressure gave a colorless liquid of rotation $+46.2$ to $+46.6^\circ$ and d_4^{25} of 0.857 to 0.855. Gildermeister and Hoffmann³ record for *d*- α -pinene from Greclan turpentine $d_4^{25} = 0.854$. The thermal rate of samples of the same pinene was observed in the gas phase by a method similar to that used by Smith.⁴ The temperature was that of boiling *p*-nitrotoluene (237°) and the values of k_1 obtained were 3.03×10^{-3} and 2.91×10^{-3} min.⁻¹, being in good agreement with Smith's value of 3.07×10^{-3} 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 nitrogen was then bubbled through the liquid through the tube C for about ten minutes to displace all of the air in the vessel. The stopcock was then closed and the system connected to the nitrogen 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 G₁ and two jets of air G₂ 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 four to eight 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.

Results.—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; it is to be noted that a slight decrease was observed in all four runs but 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 Col. 9, 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 Col. 8, were obtained by determining the rate at the boiling point, 156° , and then extrapolating down over the small temperature interval involved using Smith's value of the heat of activation, 43,710 cal./mole. The rate at the boiling point was determined experimentally by keeping pinene at 156° in an atmosphere of nitrogen for periods of twenty-four hours. The rate thus found, $k_1 = 1.90 \times 10^{-6}$ min.⁻¹, was about

³ Gildermeister and Hoffmann, "Die ätherischen Öle," Schimmel and Co., Leipzig, 1910, Vol. I, p. 305.

50% higher than that obtained by a direct extrapolation of Smith's data using his rate for the liquid at 184.6°.

TABLE I
RESULTS OF EXPERIMENTS

Run	Furnace temp., °C.	Liquid temp., °C.	Time, min.	α_1	α_2	$\Delta\alpha$	$k_1 \times 10^4$ (min. ⁻¹)	$\Delta\alpha$ (calcd.)
1	792-823	143	260	+46.74°	+46.73°	-0.01°	0.383	-0.01°
3	837-844	152	245	+46.71°	+46.70°	-.01°	1.17	-.03°
4	846-857	154	318	+46.70°	+46.65°	-.05°	1.50	-.04°
5	844-858	150	500	+46.64°	+46.60°	-.04°	0.918	-.04°

Determination of the Intensity of the Radiation

The 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 Daniels⁸ by absorbing the energy in a solution of copper chloride and measuring the rise in temperature produced. Coblenz⁹ has shown that a 2-cm. layer of 2.5% cupric chloride solution will absorb practically all of the energy in the spectral region lying at longer wave lengths than 0.6 μ . Accordingly the furnace was set in position as for a run and a stream of cupric chloride 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° while the average temperature of the air blast was 38.2° and the time of flow for 500 cc. was 518 sec., giving a flux of 527 cal. per minute. The average of eight such experiments was 535 cal. per minute with a maximum deviation of 28 cal.

The effective black-body temperature of the furnace was then estimated by assuming some temperature and calculating from the geometry of the set-up and the transmission losses the corresponding flux in 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 by¹⁰

$$F_v = \frac{1}{2D^2} c u_v T_v \left(\frac{D^2}{2} + d^2 - d \sqrt{D^2 + d^2} \right) \quad (1)$$

⁸ Coblenz, *Bulletin of the Bureau of Standards*, 9, 110 (1913).

¹⁰ J. W. T. Walsh, "Photometry," Constable and Co., London, 1926, p. 104.

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 was then obtained by graphical integration of Equation 1 over all values of ν using for u_ν the values given by the Planck radiation law, assuming a temperature of 800° , and for T_ν values obtained from Coblenz's¹¹ data on the transmission of mica.

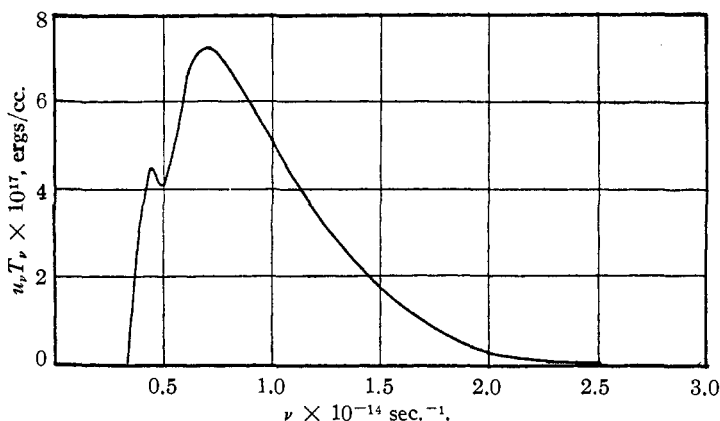


Fig. 2.—Transmitted energy distribution curve.

A plot of $u_\nu T_\nu$ against ν is shown in Fig. 2. The area under the curve was found to be 1.408×10^{-10} cal. per cc.

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

$$F_\nu d\nu = 3.19 \times 10^9 u_\nu T_\nu d\nu \text{ per sq. cm. per second} \tag{2}$$

$$F_{\text{total}} = \pi D^2/4 \times 3.19 \times 10^9 \times 60 \int_0^\infty u_\nu T_\nu d\nu = 529 \text{ cal. per min.} \tag{3}$$

Since the observed value was 535 cal. per min., it seems fair to treat the furnace as a black-body emitting at 800° , especially as the actual temperature over the greater part of the furnace was $40\text{--}50^\circ$ above this, the temperature near the open end dropping to about 750° .

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.

¹¹ Coblenz, "Investigations of Infra-red Spectra," *Carnegie Institution Publication Number 65, 1907*, Vol. III, p. 49.

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

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

where α is the absorption coefficient and x_1 the thickness of absorbing material.

Taking Coblenz's¹¹ data on pinene, the absorption coefficients α have been calculated at intervals over the range from 1 to 9μ , and, using these, values of \bar{I}/I_0 obtained from the above equation.

The flux of energy through the lower surface of the liquid is given by Equation 2: Making a correction for the slight divergence of the beam, multiplying by the average intensity ratio and dividing by the velocity of light, we get for the average radiation density of the frequency ν the expression

$$\bar{u}_\nu = 2.57 \times 10^8 \frac{u_\nu T_\nu \bar{I}}{c I_0}$$

Table II shows the values of \bar{u}_ν over the frequency range corresponding to wave lengths from 1 to 5.5μ , and also the values of the radiation density u_ν at 152° corresponding to the temperature of the liquid, the latter values being calculated from the Planck radiation law.

TABLE II
VALUES

$\lambda(\mu)$	$\nu \times 10^{-14}$	$\bar{u}_\nu \times 10^{19}$	$u_\nu \times 10^{19} (152^\circ)$
1	3	7.4×10^{-4}	3.69×10^{-9}
1.2	2.5	8.98×10^{-3}	3.84×10^{-7}
1.5	2	0.148	8.09×10^{-6}
2.0	1.5	0.805	9.85×10^{-5}
2.5	1.2	1.027	0.142
3	1	0.456	0.803
3.5	0.858	0.217	2.49
4	0.75	0.833	5.48
5	0.6	1.19	15.5
5.5	0.546	0.733	21.6

Figure 3 shows a plot of \bar{u}_ν and $u_\nu(t = 152^\circ)$ 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. The range of greatly increased intensity includes the red end of the visible 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 . 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.

Discussion

The results obtained here show that radiation in the infra-red out to a wave length 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° 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 .^{11,12}

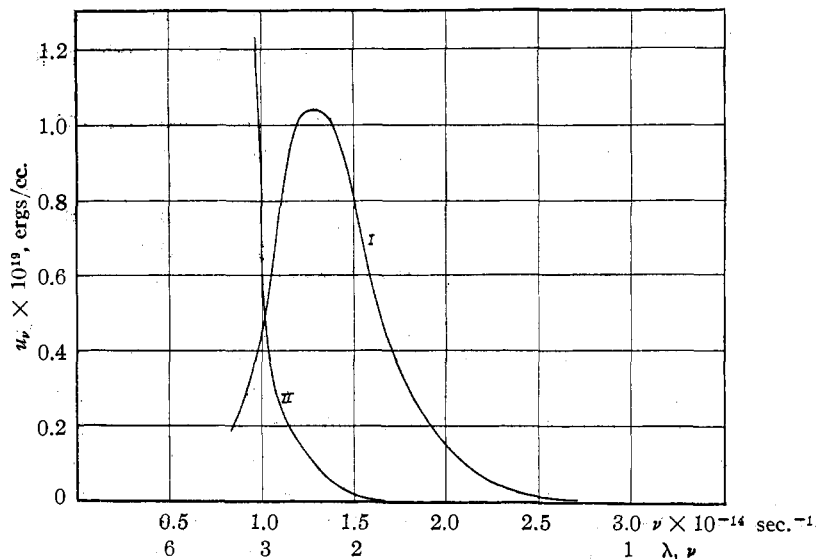


Fig. 3.—Energy distribution in liquid layer. I, Energy from furnace (\bar{u}_ν). II, Black-body energy at 152° .

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 of 13μ . The method of treatment used by them, however, seems to require some further analysis. Under the conditions of their experiment, pinene coming from a nozzle at a temperature of 93° 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 these data by the method which has been applied to the experiment just described, one may first ask the following question. By what factor is it necessary to increase the thermal reaction rate at 93° in order that it

¹² Daniels, THIS JOURNAL, 47, 2856 (1925).

may be observable during the time of exposure? Mayer has calculated that the minimum rate which he could have observed is $k_1 = 431 \text{ sec.}^{-1}$, which would be the thermal rate at 800°K . By using the value here given of the reaction rate at 156° and extrapolating in the usual manner, one finds the thermal rate at 93° 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° . 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

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

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 states which they have at 93° , then radiation has been proved to be inactive in this experiment only for wave lengths shorter than 0.79μ .

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° throughout a considerable portion of the length of the furnace. For the number of quantum jumps per second from a lower state i to a higher state j , we have the quantity $B_{ij}u_{\nu ij}$ where B_{ij} is Einstein's coefficient of absorption and $u_{\nu ij}$ is the radiation density at the frequency necessary to transfer the molecule from state i to state j . From correspondence principle considerations¹³ a maximum value of B_{ij} can be given as of the order of 10^{20} c. g. s. units;¹⁴ and taking

¹³ See Tolman, "Statistical Mechanics with Applications to Physics and Chemistry," Chemical Catalog Co., New York, 1927, p. 179.

¹⁴ 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 from absorption data values of 10^{14} to 10^{19} have been obtained. Tolman, *Phys. Rev.*, **23**, 693 (1924).

the maximum intensity in the black-body spectrum at 1073°K.¹⁵ we should have $u_{vij} = 9.75 \times 10^{-17}$ ergs-sec. per cc., giving us about 10^4 jumps per second as the maximum possible number that could take place for any given absorption line. Thus in the 1.2×10^{-4} seconds taken to pass through the furnace a molecule could not make more than one jump on the average for each absorption line that it had in the neighborhood of the maximum intensity of radiation; while the number of jumps for lines of other frequencies would be even less. If this be so, the distribution of molecules among the energy states throughout the whole length of Mayer's tube may not have been appreciably different from that prevailing at 93°.

Hence Mayer's experiment has not proved the ineffectiveness of radiation out to 13μ in the *thermal* racemization of pinene, but has 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° 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,¹⁶ as was done in the present experiments.

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 out 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 criticized 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 out as far as 13μ is inactive in the thermal racemization of pinene.

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¹⁵ The temperature used here is slightly higher than that given by Mayer. It is, however, more favorable to a high rate of activation and was used since data at this temperature were available.

¹⁶ Compare Tolman, *THIS JOURNAL*, **47**, 1549 (1925), and ref. 13, p. 283.