sociate completely on melting than there is between metals and non-metals in the periodic table.

The writer wishes to thank Mr. E. F. Salchow, who took the photomicrographs, and Mr. R. S. Dean, under whose direction the work was performed and whose advice and suggestions made the paper possible.

Summary

A pseudobinary line is defined as the line connecting the point, representing a compound between two constituents, with the third constituent in a ternary system. Experimental evidence is given to show that mixtures corresponding to compositions on this line do not behave like an ordinary binary system. Photomicrographic as well as analytical evidence is used to show that solid-solution formation may proceed at the expense of a weak metallic compound.

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

THE RATE OF RACEMIZATION OF PINENE. A FIRST-ORDER, HOMOGENEOUS GAS REACTION

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During a recent discussion by Professor G. N. Lewis and the author it was suggested by Professor Lewis that a racemization reaction would present novel features from the standpoint of theories of chemical reaction. Thus it is a reaction without heat effect and is perfectly symmetrical, the corresponding forward and reverse rates being equal. Also, the mechanism of inversion from one optically active isomer to its mirror image is easy to interpret in terms of our ideas of activated molecules, an active molecule in this case presumably having an equal chance of changing to the one or the other isomer. The course of the reaction is easily followed by measuring the rotation of the plane of polarized light produced by the mixture of the isomers.

Most racemizations that have been studied have been of polar substances (acids or bases in many cases) whose inversions usually are subject to catalysis or other complications due to ionization. Moreover, a racemization *rate* in the gas phase has to my knowledge never yet been measured. The type of reaction most interesting from the standpoint of the development of theories of reaction rate is a first-order homogeneous, gas reaction which is uncatalyzed by the walls of the containing vessel or otherwise. Thus far we have only two reactions approximating to this type.[2,3]

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[1] National Research Fellow in Chemistry.

[2] (a) Daniels and Johnston, THIS JOURNAL, **43,** 53 (1921). (b) Lueck, *ibid.,* **44,** 757 (1922).

[3] Smith, *ibid.,* **47,** 1862 (1925).

Pinene, the substance which the author of the present work chose to study, presents many advantages. Being an unsaturated substance its bonds are more or less mobile, and it would be expected to racemize at a temperature low enough to avoid carbonization. It is a non-polar substance, is fairly stable with respect to reactions other than racemization, has a moderately low boiling point (156°) and can be obtained readily.

Formulation of Expressions for Racemization Rates

It will be of advantage before describing the experimental work to formulate the equations representing the course of a simple racemization reaction. We will assume a reaction

$$A \rightleftharpoons A' \qquad (1)$$

where A and A′ are optical isomers which are transformed the one to the other by first-order reactions. At every temperature in a condition of equilibrium there will be equal amounts of A and A′. Therefore we have $K = k/k' = 1$, where K is the equilibrium constant of the reaction and k and k' are the forward and reverse reaction-rate constants, respectively. We thus have for the rate of decrease of the concentration of A

$$-dc/dt = kc - k'c' = k(c - c') \qquad (2)$$

where c and c' are the concentrations of A and of A′ at any time t. If c_0 and c_0' are the respective initial concentrations of A and A′, we have

$$c' = c_0 - c + c_0' \qquad (3)$$

Substituting Equation 3 in 2, we have

$$-dc/dt = k(2c - c_0 - c_0') \qquad (4)$$

Noting that for any given experiment, c_0 and c_0' are constants and integrating Equation 4 between the limits t_1 and t_2, we have

$$\ln \frac{2c_1 - c_0 - c_0'}{2c_2 - c_0 - c_0'} = 2k(t_2 - t_1) \qquad (5)$$

where c_1 and c_2 are the concentrations of A at the times t_1 and t_2.

When we measure in a polarimeter the rotation of the plane of polarized light produced by a mixture of the two isomers taken from the reaction at the time t_1, the rotation is a measure of $c_1 - c_1'$, since the two isomers have equal and opposite effect on the rotation. We have, however, in the reaction, at the time t_1

$$c_1 = c_0 - (c_1' - c_0')$$

or

$$c_0 + c_0' = c_1 + c_1' \qquad (6)$$

Substituting Equation 6 in 5, we have

$$\ln \frac{c_1 - c_1'}{c_2 - c_2'} = 2k(t_2 - t_1) \qquad (7)$$

or, if α is the measured angle of rotation

$$\ln \alpha_1/\alpha_2 = 2k(t_2 - t_1).$$

Thus, if we are dealing with the simple type of racemization reaction outlined above, measurements of the optical rotation of the reacting mixture at the times t_1 and t_2 are sufficient to determine the value of k. Furthermore, the only objectionable impurities in the substance measured would be other optically active substances racemizing at nearly the same rate as that of the substance under investigation, or impurities having a catalytic effect. Other optically active substances present and remaining unchanged during the course of an experiment can be corrected for when their amount is known.

Experimental Part

The measurements were made in a very simple manner. A quartz compensating polarimeter which permitted reading to 0.01° or slightly less was used. In the case of solutions a reading of the rotation was made before placing the sample in the constant-temperature bath, and upon removing and cooling to room temperature after appropriate length of time in the bath. The reaction in all cases was slow enough and the time of reaction long enough to make negligible the time of heating and cooling. Moreover, the time taken by the sample to come up to temperature was at least partially compensated for by the time taken to cool. In the case of gas reactions, the pinene was weighed into a small, thin glass tube which was subsequently placed inside a glass bulb, the bulb evacuated and sealed, and the tube of pinene then broken by shaking. After reaction, benzene was weighed into the pinene in the bulb to give enough solution for use in the polarimeter tube. Subsequently a solution of the same weight proportions of original pinene and benzene was made up and measured. At all times the pinene was kept out of contact with air on account of the danger of slight oxidation.

Constant temperatures were obtained in the case of Expts. 3–7 in Table I by the use of a thermostat filled with heavy oil, and in the other experiments by boiling various organic liquids in well lagged boiling tubes. The thermostat temperatures were read by means of a 10-junction copper-constantan thermocouple checked at the following boiling points at standard pressure: aniline, 184.4°; naphthalene, 217.9°. The calibrations at other temperatures were determined by comparison with the results for thermocouples of this type as determined by L. H. Adams.[4] The thermostat had the advantage that several experiments could be run at the same time under identical conditions.

Liquid petrolatum was chosen as the most suitable solvent for the pinene in the solution reactions, because it is stable and non-polar and has a high boiling and low melting point. The sample used had a slight optical activity which trials showed not to change during the course of an experiment at these temperatures. The measured optical rotation of the petrolatum was merely substracted from the measurements of the

[4] Adams, *Bull. Am. Inst. Mining Met. Eng.*, **43**, 2111 (1919).

pinene solutions. To show that the presence of optically active compounds in the solvent did not affect the pinene, an experiment was made using α-methylnaphthalene as a solvent.

In none of the pinene experiments did appreciable carbonization occur. Fractionation of the sample of pinene (which had a boiling-point range of 2° or 3°) did not result in a product having a different rate, so that we may conclude that the pinene used was of sufficient purity for the present purpose. It was intended to make experiments with *l*-pinene as a check on the results, but no satisfactory samples of *l*-pinene could be obtained. Most of the samples examined had a precipitate of resinous material and had a boiling-point range of some 50°.

The experimental data are presented in Table I. Col. 3 gives the initial and final polarimeter readings in the units in which the scale on the instrument was graduated, namely, 1 scale unit = $^1/_3$ degree of arc. Col. 4 gives the elapsed time; Col. 5, the calculated values of the reaction-rate constant in reciprocal minutes. The calculation of k was made as outlined above. Col. 6 gives the concentration of the pinene in terms of grams of pinene per liter under the conditions obtaining in the experiments. A pressure of 1 atmosphere at 218° would be produced by 3.38 g. of pinene per liter. The last column states whether the reaction took place in the gas phase or in a solution.

Table I

Experimental Data

Expt.	T, °C.	Polarimeter readings	Time, min.	10^5k, min.	Concentration	Remarks
1	184.5	30.23–22.40	6810	2.20	4.73	Gas
2	184.6	115.4 –76.4	6900	2.99	860.0	Pure liquid
3	197.8	31.1 –19.5	2747	8.50	3.81	Gas
4	198.0	13.69– 8.66	2650	8.64	0.79	Gas
5a	197.8	42.6 –25.8	1968	12.74	172.0	Petrolatum soln.
5b	197.8	42.6 –21.1	2734	12.84	172.0	Petrolatum soln.
6	197.8	20.4 –10.1	2738	12.83	86.0	Petrolatum soln.
7	198.0	9.33– 4.64	2649	13.18	43.0	Petrolatum soln.
8	217.7	32.75–18 01	579	51.7	5.12	Gas
9	217.9	29.51–15.59	587	54.3	4.50	Gas
10	217.7	25.5 – 1.72	2885	46.7	3.87	Gas
11	217.9	22.3 –11.43	433	78.2	86.0	Petrolatum soln.
12	217.5	24.55–13.80	360	80.0	86.0	Acetophenone soln.
13	218.0	33.06–19.65	299	87.0	129.0	α-*m*-Naphth. soln.
14	230.8	30.64– 8.74	371	169.0	4.67	Gas
15	232.3	12.95– 8.05	120	198.0	5.00	Gas
16	237.0	23.22– 6.15	216	307.0	3.63	Gas

Discussion of the Experimental Work

It is seen from Table I that the rate of reaction in solutions of acetophenone, α-methylnaphthalene, petrolatum and in the pure liquid is in general about 50% larger than the rate in the gas phase. However, the rate is the same in Expt. 3 as in Expt. 4, although the pressure in the latter was less than one-fourth as great as in the former. Moreover, Expts. 5a and 5b show that the rate varies directly as the concentration of pinene throughout a single experiment. The fact that the rate is so nearly the same in solution and in the gas phase shows the absence of wall catalysis. Since the constants are nearly the same when the concentration is varied over 1000-fold from the gas to the pure liquid reactions, we may be reasonably certain that we have here a true first-order reaction. In the case of nitrogen pentoxide solutions the rates in chloroform were on the average 50% higher than in the gas phase, and in carbon tetrachloride 28% larger. Moreover, the concentration of the nitrogen pentoxide in the solutions, as nearly as could be judged from the data presented, was not nearly as great as the concentrations of pinene in the solutions in this work. This effect is doubtless due to the influence of the fields of neighboring molecules upon the reacting molecules. The fact that the rate in solution is substantially independent of concentration and solvent is in line with this view. Whether the effect is to alter the configuration of the reacting molecules so as to require a different energy of activation is not certain.

In Table II are presented the final experimental results of the reactions in the gas phase. In Col. 4, marked ΔT, are given the values of the difference in temperature between the two experiments marked as indicated in the subscript to the values of ΔT. Col. 5 gives the values of the heat of activation calculated from the Arrhenius equation $Q = [RT_1T_2 \text{-} ln\ (k_{T_2}/k_{T_1})]/\Delta T$, where k_{T_2} is the rate constant at the temperature T_2, and k_{T_1} that at the temperature T_1. The values of Q are calculated from the two experiments indicated in the subscripts of the corresponding ΔT's. As best value of Q we give the average of the first two and the last three values in Table II, since the temperatures 184.4° (the boiling point of aniline), 217.9° (the boiling point of naphthalene) and 237° (the boiling point of quinoline) were those best known.

TABLE II

HEAT OF ACTIVATION FROM BEST VALUES OF k

Result	Temp., °K.	Rate constant 10^5k, min.	ΔT	Heat of activation (calcd.)
a	457.6	2.20	13.4 ab	43,440
b	471.0	8.57	19.9 bc	42,040
c	490.9	53.0		
d	503.9	169.0	13.0 cd	43,810
e	505.4	198.0	14.5 ce	44,780
f	510.1	307.0	19.2 cf	45,490
			Best value	43,710

The fact that the results obey so well the laws of reaction rate applying to the simple racemization process outlined above is presumptive evidence that the reaction is of this type. However, the generally accepted structural formula for pinene contains two optically active carbon atoms which make possible four isomeric pinenes formed by changes in configuration of the groups about these two atoms. These two groups are not equivalent and therefore complete internal compensation of optical activity is not possible. Since the difference in energy between these two possible isomers doubtless is considerable, they would not be readily convertible the one into the other at moderate temperatures, and at equilibrium could not be present in comparable amounts. Also, since the literature lacks mention of these particular isomers, we feel justified in concluding that only two of these four possible isomers exist. (These isomers are not to be confused with the well-known isomers designated as α-, β-pinene, etc.) It is reported, on the other hand, that prolonged heating at high temperatures changes pinene into the substance dipentene, which is supposed to be the racemic modification of limonene. Pure, synthetic pinene is the racemic modification of pinene (*dl*-pinene), simple racemization having always occurred during the reactions taking place in the synthesis.

In the present work experiments bearing on this were undertaken. The partially racemized mixture obtained from the pure liquid pinene of Expt. 2 was subjected to distillation. The boiling point of the mixture was about 4° higher than that of the original mixture. The first part of the distillate had an optical activity 20% higher than that of the mixture. The best explanation of these facts has seemed to us to be that a small fraction of the changes of one active variety of pinene to the opposite variety is accompanied by rearrangement of the molecule to form a higher-boiling substance which, judging from the literature, should be limonene. The possibility that the pinene changes to a steric isomer seems unlikely on the following grounds. First, this isomer has never been reported. Second, the present work shows that racemization taken almost to completion (see Expt. 10) yields rate constants very nearly the same as those from other experiments, indicating that the final product is a racemic mixture of the substances mainly formed in the first part of the reaction. Further, although the above laws of reaction rate would apply to a case where the reaction all went to some isomer of negligible optical activity and higher boiling point, the boiling point of any possible resulting product would doubtless be much higher than is actually the case and, also, the first fraction of the distillate should approximate the original pinene in optical activity—which it does not.

The possibility that the rise in boiling point during racemization is due to polymerization of the pinene to form diterpenes is excluded because this would be a bimolecular reaction and at the very high concentration in Expts. 2, 5 or 13 the amount of polymerization would be enormously greater than in a gas reaction at atmospheric pressure. An experiment at atmospheric pressure in a large container in an electric oven showed that the products of the gas reaction have about the same increase of boiling point as in the case of the reaction in the highly concentrated liquid phase. For example, an experiment was run at about 250° in a 2-liter flask containing 15 g. of pure pinene gas. The rotation during four and one-half hours decreased from 116 to 9 units. The first fraction of the distillate measured 17 units and the increase in boiling point was about 10°. The use of the rotation measured for the distillate would make the rate constant about 25% less. The rotation of the distillate, however, is but 15% of the original rotation and the boiling point of the mixture obtained even at this elevated temperature is but little greater than was the case in Expt. 2.

The conclusion is, therefore, that the reactions studied in this work consist for the most part in the simple racemization as assumed in the first part of this paper. Due to the small amount of disturbing side reaction, the rate constants here presented may be slightly in error. However, since the constants at the different temperatures would probably be in error by the same fraction, the temperature coefficients here presented are probably not much in error. Further work which would permit us to correct the rate constants for this side reaction was prevented on account of the termination of the author's fellowship and the lack of opportunity for further work.

Theoretical Discussion

It is of interest to compare the results of the present experiments with the predictions from the equation $k = \nu e^{-Nh\nu/RT}$, which is the form of equation first proposed by Dushman[5] and later deduced by Lewis and Smith[6] from different considerations. The value of $Nh\nu$ in this equation is, of course, equal to the Q in Table II, h is Planck's constant and e is the natural logarithm base. The value of ν corresponding to $Q = 43{,}710$ cal./g. mol. is 4.60×10^{14} sec.$^{-1}$ The value of k at 490.9° K. is calculated to be 1.54×10^{-5} in reciprocal seconds. The experimental value of k at this temperature is 0.88×10^{-5} in reciprocal seconds. This is the same order of agreement as in the case of nitrogen pentoxide,[7] and the calculated value is in both cases larger than the experimental value.

If we take the view that the fraction of molecules which are activated is equal to $e^{-Q/RT}$ and that the factor determining the rate of the reaction is the life of an activated molecule, we see that the life of an activated molecule of nitrogen pentoxide and that of pinene are about the same. If we do not take this view, or if the conclusion to which this view leads, namely, that the life of activated molecules of the very dis-

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[5] Dushman, THIS JOURNAL, **43**, 397 (1921).

[6] Lewis and Smith, *ibid.*, **47**, 1508 (1925).

[7] Tolman, *ibid.*, **43**, 269 (1921).

similar substances nitrogen pentoxide and pinene are nearly the same, seems improbable, we are forced to the conclusion that the rate of reaction is determined by the rate of activation. This is the view to which we are led from a consideration of Lewis and Smith's deduction of this equation.

Summary

1. The rate of racemization of *d*-pinene, both in solution and in the gas phase, has been measured between the temperatures 184° and 237°, and the reaction has been shown to be a simple unimolecular one. This is the first time to the author's knowledge, that a racemization *rate* has been measured in the gas phase.

2. The rates measured in the gas phase, in the pure liquid and in the solvents petrolatum, acetophenone and α-methylnaphthalene over a concentration range of more than 1000-fold, are nearly the same.

3. Evidence is introduced to show that the reaction is mainly a simple racemization and that side reactions come in but to a small extent. The actual rates may be slightly in error but the temperature coefficient is doubtless nearly correct.

4. The heat of activation as calculated from the Arrhenius equation is 43,710 cal. per gram molecule. The value of ν corresponding to this is 4.60×10^{14} sec.$^{-1}$

5. The results show approximate agreement with the equation $k = \nu e^{-Nh\nu/RT}$. The significance of this agreement is briefly discussed.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

INFRA-RED ABSORPTION SPECTRA
II. THE CHLORO-ACETIC ACIDS

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A relation between molecular structure and infra-red absorption spectra was emphasized in a recent publication from this Laboratory.[1] It was shown that completely non-polar molecules such as diatomic hydrogen do not exhibit absorption bands in the near infra-red, and it was reasoned that the progressive increase in polarity of the chloro-acetic acids with increased substitution of chlorine might be reflected in a shift of some band in the near infra-red absorption spectrum.

The present communication is concerned with the description of such a shift. It was found that the band falling at 5.90 μ in acetic acid, moves approximately 0.05 μ toward the shorter wave lengths for each chlorine atom substituted into the methyl group.

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[1] Daniels, THIS JOURNAL, **47,** 2856 (1925).