although hydrogen chloride did lead to some increase in rate. The synthetic acid may, of course, have contained some chain-stopping impurity to a greater extent than the presumably less pure commercial acid.

Chlorine and bromine bring the reaction to a dead stop. Presumably, they react with tertiary carbonium ions with the formation of tertiary halides and cut the chain length drastically. The chain length with pure chlorosulfonic acid must be long since the loss of rotation follows first-order kinetics to large losses in rotation.

Below 30°, chlorosulfonic acid and chloroform are miscible. No reaction is observed in such a solution in several days at room temperature. A mixture of chlorosulfonic acid (1.4 parts), chloroform (3 parts) and (+)3-methylhexane (1 part) is also homogeneous at 0° and 25°. However, the mixture becomes orange and evolves sulfur dioxide. After a reaction period at 0°, such a solution was neutralized with alcoholic potassium hydroxide at −33° and washed several times with cold, concentrated sulfuric acid. Upon treatment of the acid-washed material with alcoholic silver nitrate, a dense, white precipitate was formed. The filtered solution was washed with sulfuric acid to remove alcohol. With a reaction period of ten minutes at 0° negligible change in rotation occurred; in one hour, the rotation of the chloroform–hydrocarbon solution declined from 1.44 to 1.21°.

The failure of a reaction of long chain length to occur may be associated with the decreased dielectric constant of the medium and with reaction of any carbonium ions with either chlorosulfonic acid or chloroform to form the tertiary chlorides which appear to be present.

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EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Equilibrium in the System 2- and 3-Methylhexane and in the System 2,3- and 2,4-Dimethylpentane

BY LUCIEN G. MAURY,[1] ROBERT L. BURWELL, JR., AND RICHARD H. TUXWORTH

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Equilibrium constants for the reactions 3-methylhexane $\rightleftarrows$ 2-methylhexane and 2,3-dimethylpentane $\rightleftarrows$ 2,4-dimethylpentane, are: 1.47, 1.48 (60°); 1.69, 2.40 (0°); and 1.90, 2.68 (−33.4°). These values were determined by direct equilibration employing sulfuric acid at 60°, chlorosulfonic acid at −33.4° and an equimolar mixture of the two at 0°.

Sulfuric acid and chlorosulfonic acid specifically interconvert methylalkanes.[2–4] Change of chain branching as in the conversion of the 2- and 3-methylhexane pair to the 2,3- and 2,4-dimethylpentane pair occurs much more slowly. It, thus, seemed desirable to test the applicability of this discovery to the determination of the equilibrium constants of the following two reactions by direct equilibration

$$\text{3-methylhexane} \rightleftarrows \text{2-methylhexane} \qquad (1)$$

$$\text{2,3-dimethylpentane} \rightleftarrows \text{2,4-dimethylpentane} \qquad (2)$$

Voorthuijsen[5] determined the equilibrium constants of these reactions by direct equilibration of all heptanes by aluminum chloride at 20°. The more specific nature of the reaction with sulfuric acid offered hope of increased accuracy. The equilibrium constants have accordingly been measured at 60, 0 and −33.4°.

Experimental

The preparation of the hydrocarbons has been described.[3] The infrared absorption spectra were indistinguishable from those of the Bureau of Standards standard samples and no ultraviolet absorption was exhibited at wave lengths longer than 2200 Å.

As isomerizing agents, 96.04% sulfuric acid was employed at 60°, an equimolar mixture of this acid and freshly distilled Eastman Kodak Practical Grade chlorosulfonic acid was employed at 0°, and the chlorosulfonic acid alone was employed at −33.4°. Thermostating was by a water-bath at 60°, by an ice–water mixture at 0° and by refluxing ammonia at −33.4°.

The value of the equilibrium constant was first approximated from the relative *initial* rates of isomerization of the two hydrocarbons by the relation $K = k_1/k_{-1}$. Mixtures of known composition on either side of the estimated equilibrium composition were prepared and subjected to the isomerizing conditions. According to the observed changes in composition, the estimated equilibrium composition was revised and new mixtures prepared. These were then subjected to isomerizing conditions. By this means, it was possible to employ short times of contact and relatively mild condition and, thus, to minimize side reactions.

Reaction flasks and stirring procedures have been described.[3] To avoid preferential vapor loss of one component, ratios of gas to liquid volume were kept low, never exceeding 15 to 1.

The flask and acid were brought to temperature before the hydrocarbon mixture was added. After "emulsification" by magnetic stirring for the desired time, stirring was stopped and a sample of the hydrocarbon layer was pipetted into a cold 30% solution of potassium hydroxide. The hydrocarbon layer was then removed and stored over solid potassium hydroxide before analysis. Precautions were taken throughout to prevent change in composition of the hydrocarbon sample after removal from the thermostated reactor either by isomerization or preferential vapor loss.

Analysis.—An infrared spectrometric technique was employed[3] using a pair of matched cells and substitution against a standard mixture. As appropriate, this was

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[1] Standard Oil Company (Indiana) Fellow, 1950–1951.

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[3] R. L. Burwell, Jr., Robert B. Scott, Lucien G. Maury and Allen S. Hussey, *ibid.*, **76**, 5822 (1954).

[4] R. L. Burwell, Jr., Lucien G. Maury and Robert B. Scott, *ibid.*, **76**, 5828 (1954).

[5] J. J. B. Voorthuijsen, *Rec. trav. chim.*, **66**, 323 (1947).

59.18 mole % of 2-methylhexane and 40.82 mole % 3-methylhexane or 62.13 mole % 2,4-dimethylpentane and 37.87 mole % 2,3-dimethylpentane. In the first system, measurements were made at 7.43, 8.63, 10.43, 11.09 and 12.98 μ; in the second, at 8.68, 9.02, 9.96, 10.46, 12.38 and 12.78.

In the methylhexane system, a plot of log % transmission *vs.* % 2-methylhexane was prepared at each of the five wave lengths. The standard mixture was always in Cell A and the transmission was always adjusted to read 100% with Cell A in the beam. The plots were prepared from readings with the various synthetic mixtures prepared for isomerization runs in Cell B. Average deviations from smooth curves were less than 0.1%. Synthetic mixtures could be analyzed to this accuracy at all wave lengths. With products of isomerization runs, particularly those extending over longer periods of time, there was some spread in the values determined for each wave length owing to products of side reactions.

Results and Discussion

By exposing mixtures of hydrocarbons in the vicinity of the equilibrium mixture to isomerizing conditions for relatively short times, the position of the steady state has been located with minimum interference by side reactions. We feel that the position of the steady state, so located, is accurate to within several tenths of 1%. The experimental data are shown in Tables I and II.

TABLE I

THE 2-METHYLHEXANE–3-METHYLHEXANE EQUILIBRIUM

Temp., °C.	Reacn. time, hr.	Reactant mixture, % 2-methylhexane	Product mixture, av. % 2-methylhexane	Av. dev., %
60	1.00	56.7	58.0	0.4
	1.00	60.4	60.0	.3
	0.50	59.2	59.5	.1
	.50	59.8	59.6	.3
0	.67	65.6	64.6	.8
	.33	63.5	62.8	.4
	.25	62.7	62.8	.2
−33.4	.67	60.5	62.0	.4
	1.00	65.3	65.5	.7
	0.50	65.7	65.5	.3
	1.00	65.4	65.5	.2

TABLE II

THE 2,3-DIMETHYLPENTANE–2,4-DIMETHYLPENTANE EQUILIBRIUM

Temp., °C.	Reacn. time, hr.	Reactant mixture, % 2,4-dimethylpentane	Product mixture av. % 2,4-dimethylpentane	Av. dev., %
60	0.16	60.2	60.0	0.1
	.16	59.5	59.6	.2
	.16	59.8	59.7	.2
0	.16	70.5	70.6	.1
	.16	70.8	70.6	.1
	.16	70.6	70.6	.1
−33.4	.16	74.2	73.0	.2
	.16	71.4	72.2	.2
	.16	72.7	72.8	.1
	.16	73.1	72.9	.1

However, as Bates has pointed out,[6] in the presence of side reactions, the steady state does not necessarily correspond to the equilibrium composition. Since the interconversion of 2- and 3-methylhexane proceeds about 10 times as fast as the formation of dimethylpentanes,[3] the error introduced into the equilibrium constant is small.[5] Furthermore, at 60°, at any rate, if the mechanism advanced[3] is correct, no error is introduced, since the rate constants of reaction of each of the pair of hydrocarbons involved would be identical. The small spread in the analyses at different wave lengths (Tables I and II) suggests that no serious error was introduced by side reactions.

One group of investigators[7] has reported that 2,3- and 2,4-dimethylpentane are converted to 2,2-dimethylpentane and/or trimethylbutane nearly as fast as they are interconverted. Since such isomerization would invalidate our procedures, a sample of 2,4-dimethylpentane was agitated with sulfuric acid for slightly more than one-half life of conversion to 2,3-dimethylpentane. The hydrocarbon layer was fractionated in a spinning band column and analyzed mass spectrometrically. Traces of trimethylbutane and 3,3-dimethylpentane were reported only in the second fraction which was otherwise pure 2,4-dimethylpentane. Ignoring a first fraction of 3.5% of the total which was not analyzed because of probable presence of hexanes, the rate of conversion to 2,3-dimethylpentane is at least 100 times that of isomerization to the two hydrocarbons found in trace amounts. The report of 2,2-dimethylpentane and/or trimethylbutane probably resulted from the presence of branched-chain octanes formed by disproportionation.

Computed equilibrium compositions and constants are presented in Table III where they are compared with the values of Voorthuijsen,[5] the recent values of Roebuck and Evering,[8] and the computed values of Rossini.[9] In view of the differences in the experimental procedures, the several sets of experimentally determined equilibrium constants are in reasonable agreement. The agreement between the experimental and the calculated con-

TABLE III

EQUILIBRIUM RESULTS

Temp., °C.	3-MH = 2-MH[a]			2,3-MP = 2,4-MP[b]		
	X^{eq}_{2MH}	K	$\Delta F°$, cal.	X^{eq}_{24MP}	K	$\Delta F°$ cal.
60[c]	0.595	1.47	−255	0.596	1.48	−260
0[c]	.628	1.69	−285	.706	2.40	−475
−33.4[c]	.655	1.90	−306	.728	2.68	−470
25[d]	.56–.59	1.35	−180	.65–.66	1.90	−380
20[e]	.62	1.63	−284	.60	1.50	−236
60[f]	.51	1.05	− 29	.20	0.25	+921
0[f]	.56	1.27	−130	.22	.29	+668
−33.4[f]	.60	1.49	−191	.25	.33	+525

[a] 2-MH and 3-MH are 2- and 3-methylhexane, respectively. [b] 2,3-MP and 2,4-MP are 2,3- and 2,4-dimethylpentane, respectively. [c] Results of this investigation. [d] Roebuck and Evering (ref. 7). [e] Voorthuijsen (ref. 5). [f] Rossini, *et al.* (ref. 8).

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(6) J. R. Bates, THIS JOURNAL, **68**, 511 (1946).

(7) D. P. Stevenson, C. D. Wagner, O. Beeck and J. W. Otvos, *ibid.*, **74**, 3269 (1952).

(8) A. K. Roebuck and B. L. Evering, *ibid.*, **75**, 1631 (1953). These values were obtained by direct equilibration with sulfuric acid.

(9) American Petroleum Institute, Research Project 44 at the National Bureau of Standards, "Selected Values of Properties of Hydrocarbons," F. D. Rossini, E. J. R. Prosen and K. S. Pitzer, *J. Research Natl. Bur. Standards*, **27**, 529 (1941). The values of $\Delta F°$ for the vapor state were corrected by the Antoine Equation from the first cited reference to the liquid state assuming Raoult's Law.

stants is as good as could be expected in the case of the methylhexanes. The discrepancy in the case of the dimethylpentanes amounts to about 1000 cal. in terms of $\Delta F°$.

To within the accuracy of the data, the values of $\Delta F°$ for the methylhexane reaction are representable by $\Delta H° = -436$ cal. and $\Delta S° = +0.55$ cal./deg. Standard states are the pure liquids. The rate of change of $\Delta F°$ is rather large in the case of the dimethylpentanes. We do not have results at sufficiently closely spaced temperature intervals to permit an accurate computation of $\Delta H°$ and $\Delta S°$. $\Delta S°$ changes sign in the vicinity of 0° at which temperature, $\Delta H°$ has a value of about -475 cal.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SYRACUSE UNIVERSITY]

The Identification of Solvated Electrons and Radicals in Rigid Solutions of Photoöxidized Organic Molecules; Recombination Luminescence in Organic Phosphors[1]

BY HENRY LINSCHITZ, MYRON G. BERRY AND DONALD SCHWEITZER

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Rigid solutions of alkali metals in solvents containing methylamine show an absorption peak at 6000 Å. Upon illumination, a new band appears in the near infrared while the 6000 Å. peak diminishes. The new band is attributed to incompletely solvated electrons. This same infrared band is found in illuminated rigid solutions of easily oxidized organic molecules, indicating, in agreement with previous work of Lewis and Lipkin, that photo-ejection of electrons has occurred. Upon slight softening of the solvent, solutions of such organic molecules frequently emit light (delayed luminescence). This luminescence can be maintained for hours if the solvent viscosity is properly controlled. The phenomenon is quite general and occurs in a wide variety of molecules. Evidence is presented which establishes that the luminescence is due to triplet states arising from recombination of radicals and trapped or solvated electrons, both formed originally by photoöxidation of the parent molecule.

Among the key problems in photo-chemistry and radiation chemistry is the identification of high-energy intermediates formed during the reaction. The use of rigid or glassy solvents affords a good method for stabilizing labile products since such bimolecular processes as ion or radical recombination or dismutation may be prevented, and the unstable species studied by appropriate means. In a glass at low temperature, quenching of electronic energy by "internal conversion" to the ground state is also impeded[2,3] making it possible to identify metastable excited states by their luminescence[3,4] or even by their absorption.[3,5] The usefulness of rigid solvent techniques in studying the photochemistry and spectroscopy of complex molecules has been most clearly brought out in the beautiful work of G. N. Lewis and his school[3,4,6,7] in which a variety of photo-processes (triplet-state excitation, electron-ejection, bond dissociation) were established and studied by this means. Some peculiar luminescence effects also were observed, in addition to the well-known "normal" phosphorescence, due to triplet-singlet transitions.[8] Lewis and Bigeleisen[9] found extremely long afterglows ($\tau \sim 1$ hr.) in rigid solutions of N-lithium carbazole or diphenylamide. When the phosphor was withdrawn from the Dewar and allowed to warm up, the luminescence intensity increased many-fold, went through a maximum and finally died out as the solvent fully liquefied.[10] The work described in this paper was begun in order to extend previous studies on photo-processes in rigid solvents and, in particular, to clarify the mechanism of the "delayed luminescence" found by Bigeleisen.

The lifetime of this luminescence at liquid nitrogen temperature is far too long to be accounted for by a triplet–singlet transition of the type usually responsible for phosphorescence of aromatic organic compounds.[8] The enhancement of intensity on softening of the solvent is also contrary to experience with other organic phosphors, in which loss of rigidity causes increased thermal degradation. Since no change in the natural radiative lifetime occurs, this can only result in a diminution of intensity. It appeared therefore that the delayed luminescence was due either to a new type of transition, which was very strongly vibration-coupled, or to some type of viscosity-dependent recombination process.[11]

In the same series of studies, Lewis and Lipkin[6] showed that the illumination of many easily oxidized organic molecules (amines, phenols, dyes, etc.) in rigid solvents leads to the appearance of absorption bands which correspond to the known free radicals or semiquinones of these molecules, prepared by ordinary chemical oxidation. They therefore proposed that direct photo-ionization (or oxidation) occurs in such cases

$$R \xrightarrow{h\nu} R^+ + e^-$$

In most instances softening of the solvent by warm-

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