with two drops of concentrated hydrochloric acid and twenty volumes of acetone. The fine white needles were very soluble in water.

Anal. Calcd. for $C_6H_{30}O_3N_6Cl_3Os$: N, 15.82; Cl, 20.16; Os, 35.8. Found: N, 16.0; Cl, 20.1; Os, 35.7.

Bis-(β-aminoethylamido)-bisethylenediamine-osmium(IV) Iodide, [Os(en-H)$_2$en$_2$]I$_2$.—The pink iodide [Os(en-H)$_2$en]I$_2$ above (1 g.) in a small tube containing anhydrous ethylenediamine (1 ml.), was placed under partial vacuum (5 mm.) until about half the base had boiled away. The tube was then sealed under vacuum and heated in a boiling water-bath for an hour, when the pink solid had dissolved to an intense green solution. This solidified on cooling. The original mixture, before heating, was slightly paramagnetic due to the small moment of the pink substance (0.4–0.5 B.M.) but after heating was diamagnetic. The contents of the tube were washed out with oxygen-free absolute alcohol. With protracted washing a pink tint could be detected in the product. This could be due either to incompleteness of the reaction or subsequent dissociation. The analyses showed an Os–N ratio of between 8.7 and 7.6, and attempts to isolate a pure product were fruitless. The substance dissolved in air-free water to a green solution, which instantly turned brown with oxygen.

Anal. Calcd. for $C_8H_{29}N_8I_2Os$: N, 16.44; Os, 27.92. Found: N, 16.4, 15.4; Os, 26.5, 27.2; whence N:Os = 8.7:1 and 7.6:1.

Tris-(β-aminoethylamido)-ethylenediamine-osmium(V) Iodide Tetrahydrate, [Os(en-H)$_3$en]I$_2$·4H$_2$O.—The iodide [Os(en-H)$_2$en]I$_2$ above (2 g.), with anhydrous ethylenediamine (5 ml.) was heated at 90–100° while a slow current of *dry*, CO$_2$-free air was passed through for 20 hours. At the end of this time most of the ethylenediamine had evaporated leaving a brown resinous material, which was dissolved in 50 ml. of hot methanol and then fractionally precipitated with ether. The least soluble fractions were recrystallized from methanol and ether to yield a black micro-crystalline powder, which was dried at 98°. The substance was very deliquescent, but sparingly soluble in ethanol and acetone. Very dilute aqueous solutions were brownish green changing to light green on the addition of cerium(IV) sulfate. The perchlorate and sulfate were also very soluble in water, but were investigated further. The molar conductivity in 10^{-4} *M* solution of 252 ohms^{-1} is consistent with a bi-univalent electrolyte.

Anal. Calcd. for $C_8H_{37}N_8O_4I_2Os$: N, 14.87; I, 33.74; Os, 25.25; H$_2$O, 9.57. Found: N, 14.7; I, 33.6; Os, 25.4; H$_2$O, 9.6.

Tetrakis-(β-aminoethylamido)-osmium(VI) Iodide Trihydrate.—The most soluble fractions from the methanol/ether fractionation above were crystallized several times from methanol by adding ether, rejecting the least soluble material. The green to brown microcrystalline powder was dried at 98°. It was very deliquescent. Very dilute aqueous solutions were green, unaffected by acid solutions of Ce(IV) salts, but became brown on treatment with sodium hydrosulfite due to the formation of the Os(V) compound. The molar conductance in 10^{-3} *M* solution was 245 ohms^{-1}.

Anal. Calcd. for $C_8H_{35}O_3N_8I_2Os$: N, 15.25; I, 34.60; Os, 25.91. Found: N, 15.3; I, 34.2; Os, 25.8.

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Solubility of Isomeric Hexanes in Perfluoroheptane

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Critical solution temperatures are reported for mixtures of four isomeric hexanes with perfluoroheptane. Analysis of the values obtained indicates that the geometry of the molecule does not significantly influence the extent to which the apparent solubility parameter of the hydrocarbon exceeds the theoretical value.

It has been established that for liquid mixtures of alkanes and perfluoroalkanes the entropy of mixing is not ideal, hence that the conditions for the application of the Hildebrand regular solution equations are not met.[1] Nevertheless, it has been shown that for these solutions, the Hildebrand equations correctly represent the properties provided that an empirical solubility parameter be used for the hydrocarbon rather than the theoretical value, $(\Delta E_v/v)^{0.5}$.[1,2]

In the course of investigating the behavior of mixtures of alkanes with various non-polar substances, the critical solution temperature (c.s.t.) values for four of the five isomeric hexanes in mixtures with perfluoroheptane have been determined. These values permit some evaluation of the effect of structure of the hydrocarbon on the extent to which the empirical parameter for the hydrocarbon exceeds the theoretical value, uncomplicated by differences in molecular weight, or significant variation in molecular volume. It is also felt that complications are avoided by using for all the determinations a homogeneous sample of fluorocarbon—a small cut from the distillation of a single fluorocarbon sample. In this Laboratory, no fluorocarbon material has been purified to more than 98 mole % purity as measured by time–temperature cooling curves; therefore, comparisons of results involving different samples of fluorocarbon are subject to some doubt as to whether the impurities of the various samples are the same.

Experimental

Materials.—The alkanes used were Matheson, Coleman and Bell products, best available grades. Each sample was washed with sulfuric acid, water and potassium carbonate solution. The samples were passed through a column 0.5 m. in length packed with activated silica gel, dried over potassium carbonate, and distilled through a ten-plate column packed with stainless steel helices. A middle fraction of 100 ml. was taken for use from the 500 ml. charge. Table I summarizes the distillation data for the alkanes and perfluoroheptane. Exposed stem corrections were made on the calibrated thermometer, and the observed b.p. values corrected to 760 mm. using the data of reference (3).

The perfluoroheptane, furnished by the Minnesota Mining and Manufacturing Co., was washed with sulfuric acid, water and potassium carbonate solution. It was dried over anhydrous potassium carbonate, passed over activated silica gel in a 0.5 m. column, and refluxed four hours over bright sodium. A middle fraction of 30 ml. from a 150-ml. charge was taken for use. The value of the b.p. at 760 mm.

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(1) J. H. Hildebrand, B. B. Fisher and H. A. Benesi, THIS JOURNAL, **72**, 4348 (1950).

(2) J. A. Neff and J. B. Hickman, *J. Phys. Chem.*, **59**, 42 (1955).

(3) F. D. Rossini, *et al.*, "Selected Values of Properties of Hydrocarbons," (Circular C461) U. S. Govt. Printing Office, Washington, D. C., 1947, pp. 483.

TABLE I

DISTILLATION DATA FOR SUBSTANCES USED

Substance	B.p., °C. cor. to 760 mm.	B.p., °C., 760 mm., lit.
Hexane	68.6–68.8	68.742[a]
3-Methylpentane	63.4–63.5	63.284[a]
2,2-Dimethylbutane	50.5–50.6	49.743[a]
2,3-Dimethylbutane	58.1–58.2	57.990[a]
Perfluoroheptane	82.7–83.1	82.43[b]

[a] Reference 3. [b] J. H. Simons, "Fluorine Chemistry," Vol. I, Academic Press, Inc., New York, N. Y., 1950, p. 454.

involves thermometer corrections as stated for the alkanes; correction of the observed b.p. to 760 mm. was made by use of the data of Neff and Hickman.[2]

Critical Solution Temperatures.—Weighed samples of alkane and perfluoroheptane were sealed in clean, dry Pyrex bulbs. Unmixing temperatures were determined with thermometers calibrated against a platinum resistance thermometer standardized by the United States National Bureau of Standards. Each experimental value presented in Fig. 1 represents the average of at least ten determinations, the maximum variation of which was 0.1°.

Results and Discussion

The values of $(\delta_1 - \delta_2)$ for the systems studied were computed from the equation[4]

$$RT_c = \frac{2x_1x_2v_1^2v_2^2}{(x_1v_1 + x_2v_2)^3}(\delta_1 - \delta_2)^2$$

in which the x's represent the mole fractions of the components (at the c.s.t.) having molar volumes v_1 and v_2. R is the gas constant in calories, and T_c is the c.s.t. in °K. Because of the scarcity of available data for the density of perfluoroheptane, and since the sample available had a purity as indicated by f.p. no higher than 98 mole %, densities of the perfluoroheptane were determined at 28 and 0°, corresponding to molar volumes of 226.4 and 216.2 ml./mole. The molar volume values for the hydrocarbons were based on published data.[3] Table II, column 3, gives the results of these computations.

TABLE II

COMPUTED VALUES OF SOLUBILITY CONSTANTS

(1) Perfluoroheptane with	(2) C.s.t., °C.	(3) $(\delta_1 - \delta_2)$	(4) δapp. T_c	(5) δapp. 25°	(6) δtheo. 25°
Hexane	28.5	2.86	8.90	8.94	7.27
3-Methylpentane	18.9	2.85	8.99	8.90	7.13
2,3-Dimethylbutane	9.5	2.52	8.75	8.55	6.97
2,2-Dimethylbutane	−0.5	2.49	8.83	8.48	6.71

Column 4 of Table II represents the result of adding the difference value of column 3 to the calculated solubility parameter of the fluorocarbon at the c.s.t.—hence an arbitrary and empirical "effective solubility parameter" of the hydrocarbon (solubility parameter values for the fluorocarbon were calculated from the relationship $\delta = (\Delta E/v)^{0.5}$ using ΔE as calculated by application of the Clapeyron–Clausius equation to the vapor pressure data of Neff and Hickman[2] and molar volume values interpolated from those determined). The "apparent solubility parameter" values of column 4 are not strictly comparable one to another since they correspond to different temperatures. Column 5 represents values obtained from those of column 4 by application of the assumption that the "apparent (effective) solubility parameter" has the same coefficient of temperature change as does the parameter of the pure hydrocarbon. This assumption has been used to calculate values at 25°.

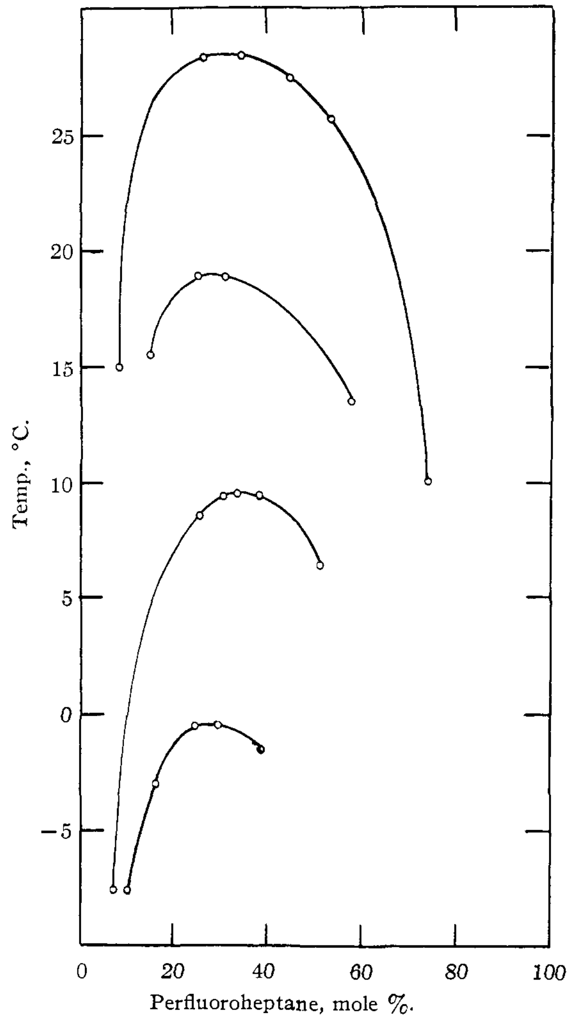

Fig. 1.—Miscibility curves for mixtures of perfluoroheptane with (from top to bottom): hexane, 3-methylpentane, 2,3-dimethylbutane, 2,2-dimethylbutane.

No strict quantitative significance is claimed for the figures of either columns 4 or 5. It must be remembered that the Hildebrand equations properly do not apply to fluorocarbon–hydrocarbon mixtures since these solutions do not meet all the criteria on which derivation of the equations was based. However, it has been shown[1,2] that there is much information relating to such solutions that may be correlated using the regular solution equations and an artificial, empirical solubility parameter for the hydrocarbon.

Column 5 gives some quantitative expression to that which is evident in examining the c.s.t. values: although a much higher parameter must be used for the hydrocarbon than that which is calculated theoretically (column 6), there is no significant change in the relationship of the parameter of one isomer to that of another—the values of column 5 are

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(4) J. H. Hildebrand and R. L. Scott, "The Solubility of Non-Electrolytes," 3rd edition, Reinhold Publ. Corp., New York, N. Y., 1950, p. 253.

1.6–1.8 units higher than those of column 6, there being no magnification of the differences between isomers in changing from the theoretical to the empirical parameters.

From this it appears that the geometry of the alkane molecule has little or no effect on the extent to which its apparent solubility parameter exceeds the theoretical value. This same conclusion is supported by examination of published data[1,2] for other mixtures of alkanes with non-polar substances.

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[CONTRIBUTION FROM NAVAL RESEARCH LABORATORY]

Rotational Isomerism in Symmetrical Dichloroacetone

BY L. W. DAASCH AND R. E. KAGARISE

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The infrared absorption spectra of liquid and gaseous dichloroacetone (1,3-dichloropropanone) have been observed in the region from 650 to 5000 cm.$^{-1}$. In addition, infrared spectra of the solid and solutions in CCl_4, CS_2 and cyclohexane have been obtained for the 270 to 5000 cm.$^{-1}$ region. The complete Raman spectrum of the liquid and a partial spectrum (300–1200 cm.$^{-1}$) of the solid have been observed. The effects of temperature, dissolution and state upon the vibrational spectrum indicate the presence of two rotational isomers in the liquid and vapor states. The more polar form, which alone persists in the crystalline solid, is also the more stable form in the liquid. The lower limit for the energy difference in the liquid was observed to be 1500 cal./mole. In the vapor, however, the less polar species is more stable, indicating a reversal in relative stability in going from liquid to gas.

Introduction

During the last two decades a variety of chemical compounds have been shown to possess rotational isomers. Such rotational isomers are possible when different stable configurations can be obtained by the rotation of end groups about a single bond. Thus one would expect a favorable condition to exist in those substituted acetones for which the C_3 symmetry of either or both end groups has been destroyed. Indeed, Mizushima and co-workers[1] have recently shown that two isomeric species are present in $CH_3{\cdot}CO{\cdot}CH_2Cl$.

This report presents the infrared and Raman spectra of symmetrical dichloroacetone (1,3-dichloropropanone) which also should have indications of rotational isomerism. To the best of our knowledge no previous spectroscopic data have been reported on this compound.

Experimental Equipment and Procedures

Materials.—Symmetrical dichloroacetone obtained from commercial sources was recrystallized from benzene and distilled under vacuum directly into the Raman sample tubes. Samples for the infrared work were taken from the recrystallized material.

Infrared Spectra.—The infrared spectra were obtained with one of three instruments depending upon the region under investigation. The 650–5000 cm.$^{-1}$ interval was studied with a Perkin-Elmer Model 21 Spectrophotometer equipped with NaCl optics. For the 450–650 cm.$^{-1}$ region the large research type instrument previously described[2] was used. Finally, a Perkin-Elmer Model 12-B instrument equipped with a KRS-5 prism was employed for the 270–450 cm.$^{-1}$ frequency range.

Studies in the region below 650 cm.$^{-1}$ were possible on the solid and solutions only, since liquid and gaseous dichloroacetone react with the KBr windows of the cells normally used in this region. The vapor spectrum was obtained using an absorption cell equipped with rock salt windows. The windows were cemented with Glyptal to a 5-cm. Pyrex glass body fitted with a stopcock. The cell proper was mounted within a heated container, also equipped with NaCl windows.

Two crystalline forms of dichloroacetone have been observed. The spectra of these modifications (needles and rhomboids) obtained with unpolarized incident radiation are very similar, and are undoubtedly polymorphs of the same isomeric species. However, their polarization spectra are distinctly different and may be useful in crystallographic studies.

Raman Spectra.—The Raman spectrometer used in this work was a commercial instrument built by the Applied Research Laboratories. This instrument records either photoelectrically or photographically with a dispersion of 15 Å./mm. at 4358 Å. Depolarization values for the stronger lines were obtained using the photoelectric portion of the instrument and the method previously described.[3] Qualitative estimates of the polarization of the weaker lines were made using the photographic portion of the instrument.

The solid sample for Raman work was obtained by progressively cooling the melted sample along the length of the Raman tube. The light scattered by the solid was such that a rather poor spectrum was obtained.

Results and Discussion

Infrared spectra of the vapor, liquid and solid states are shown in Fig. 1. The observed frequencies are listed in Table I along with the Raman data for the liquid and solid. The effects of changes of state, temperature and dilution on the infrared spectrum are listed in Table II. An examination of these data shows that certain well defined relationships exist between the effects of solidification, dilution, etc., on the individual infrared bands. First, those bands which persist in the spectrum of the solid are weak in the gas phase, increase in intensity as the temperature is lowered in the liquid phase and decrease in intensity with dilution. Second, those bands which are strong in the spectrum of the gas are absent in the spectrum of the solid, decrease in intensity as the temperature is lowered in the liquid phase, and increase in intensity with dilution.

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(3) D. H. Rank and R. E. Kagarise, *ibid.*, **40**, 89 (1950).