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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(1) S. Mizushima, S. Takehiko, M. Tatuso, I. Isao, K. Kuratani, I. Nakagawa and N. Shido, *J. Chem. Phys.*, **21**, 815 (1953).

(2) J. Rud Nielsen, F. W. Crawford and D. C. Smith, *J. Opt. Soc. Am.*, **37**, 296 (1947).

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

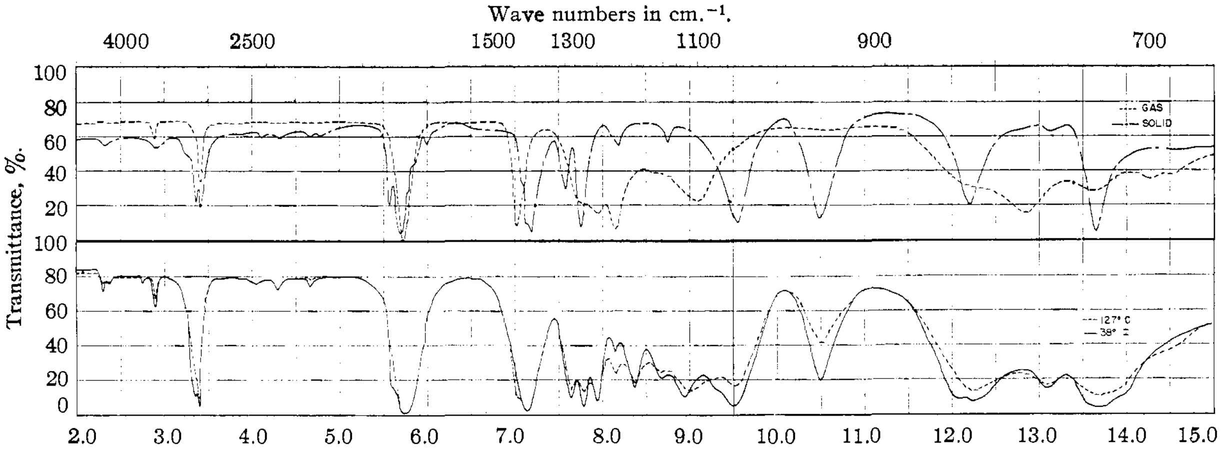

Fig. 1.—Infrared spectra of 1,3-dichloropropanone for gas and solid phases (top curve), liquid phase (bottom curve); cell length 0.05 mm.

TABLE I

INFRARED AND RAMAN SPECTRAL DATA ON 1,3-DICHLOROPROPANONE

Infrared					Raman
Gas	Liquid	Solution	Solid	Solid[a]	Liquid
3460 w	3460 w	3450 m	3450 w		
		3017 w			3017 w
	2980 ms	2980 m	2980 s		2940 s (p)
2942 ms	2940 s	2945 s	2940 s		
	1785 w	1785 w	1788 s		
1744 vs	1746 s	1754 vs	1750 vs		1743 s (p)
		1738 vs	Several weak bands		
			1665 vw		
1425 s	1420 w	1425 w			
	1398 vs	1398 vs	1398 w		1403 s (dp)
			1388 vs		
	1315 m	1302 s	1315 s		
1282 m	1282 m	1280 s	1289 s		1285 vw (dp)
1258 m	1258 m	1253 s			1250 vw (p)
1230 s	1227 m	1225 s			
			1219 w[b]	1205 m	1219 w (p)
	1192 m	1192 m		1172 ms	1178 vw (dp)?
	1146 vw	1140 w	1142 w		1140 vw (dp)?
1100 ms	1120 m	1112 s		1123 vw	
	1051 m	1045 w	1045 vw	1036 vw	1049 vvw?
	951 m	942 m	952 vs		926 vvw?
820 m	825 ms	815 s	818 s	805 vs	830 vs (p)
	812 ms				
777 s	765 ms	774 s	765 w		770 m (p)
732 m	732 s	732 s	730 s	726 m	735 s (p)
695 m	692 w	692 ms	695 vw	692 vw	692 mw
687 m					
No data	No data	631 s	634 s	645 w	634 mw (dp)
		538 s			518 vw?
		465 s			465 vw?
		378 vw			387 w?
		340 vw	339 w	301 vs	305 s (p)
			284 m		
					232 m (p)
					185 160 } m (dp)

[a] Higher frequencies in Raman spectrum overlaid with arc lines. Raman lines around 1750 and 1300–1400 cm.$^{-1}$, if present, must be considerably weakened, relative to other lines reported here. [b] In spectrum of needle-like crystals.

There are a few exceptions to these rules in the case of the dilution effects. However, it should be pointed out that the changes in intensity due to dilution were weaker and in general less reliable than those variations due to temperature changes. Certain bands where dilution information is missing in Table II had such small changes in intensity that any trends were apparently masked by such errors as the loss of solvent during transfer and dilution.

TABLE II

SUMMARY OF EFFECTS ON THE SPECTRA OF 1,3-DICHLOROPROPANONE BY CHANGING EXPERIMENTAL CONDITIONS

Frequency,[a] cm.$^{-1}$ (in liquid)	Gas	Soln. effect of diln.[b]	Liquid vs. dil. CS_2 soln.[c]	Liquid effect of temp.[d]	Solid (needle-like)
3017	−	−			
2980	−	+		−	+
2940	+				+
1785				−	+
1746	+	−		?	+
1738		+		+	
1420	+	+		+	−
1398	−	−		Too strong	+
1315	−	−		−	+
1282	+ (w)	−	−	−	+
1258	+	−?	+		−
1227	+	+	+	+	+ (w)
1192	−	−	−		−
1146	−			−	+
1120				−	−
1112	+		+	+?	−
1051	−	−		−	+
951	−	−	?	−	+
825	+ (w)	−		−	+
765	+	+	+		+ (w)
732	+ (w)	−		−	+
692	+		+	+	−

[a] Gas and solid: + = present; − = absent. [b] Dilution effect: + = increased intensity with dilution; − = decreased intensity with dilution. [c] Liquid vs. CS_2: + = increased intensity from liq. to soln.; − = decreased intensity from liq. to soln. [d] Liquid temp. change: + = increased intensity with increased temp.; − = decreased intensity with increased temp.

The experimental observations summarized above appear to be explainable in terms of either molecular association or rotational isomerism. Thus, if the liquid state consists of monomeric and dimeric molecules in equilibrium, dissolution or increasing the temperature will increase the relative abundance of the monomeric species. Moreover, in the gas phase one would expect a predominance of monomers, while in the solid state nearly complete association should occur. On the other hand, these same changes can be interpreted solely on the basis of rotational isomerism, since the relative abundance of the various isomers depends upon the temperature, state, and degree of dilution. It is necessary, therefore, to differentiate between these two phenomena.

The carbonyl stretching frequency and the C–H bending frequencies might be expected to give evidence of association if it is present. Indeed, the bands at 1738 and 1754 cm.$^{-1}$ (C=O) and 1398 and 1425 cm.$^{-1}$ (C–H bending) were profoundly influenced by dissolution in CCl_4, CS_2 and cyclohexane. The change observed in the relative intensities of these two pairs of bands was much greater than that for any other band in the spectrum. Figure 2 shows the effects of dilution in CCl_4 on the carbonyl region. However, the increase in intensity of the lower frequency (1738 cm.$^{-1}$) in the carbonyl region and the higher frequency (1425 cm.$^{-1}$) in the C–H bending region with dilution are effects which are just opposite to those predicted on the basis of association. It would seem impossible, therefore, to interpret these data on the basis of association.

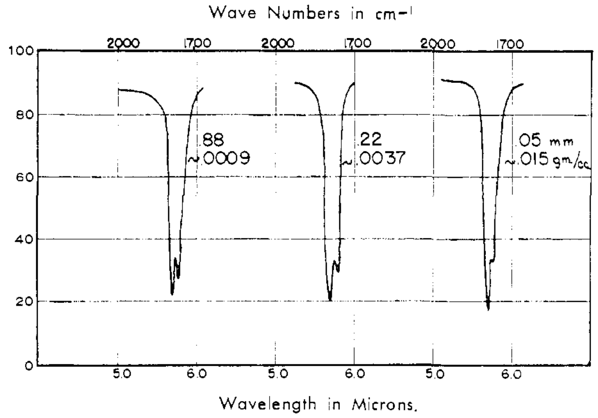

Fig. 2.—Spectrum of the carbonyl region for 1,3-dichloropropanone in carbon tetrachloride solutions. (The product of concentration × path length is essentially constant.)

Recent investigations[4–6] have shown that in solutions the apparent energy difference between rotational isomers having different dipole moments depends upon the dielectric constant of the solution. Hence, as the solution is diluted its dielectric constant approaches that of the solvent, and the relative abundance of the various isomers changes accordingly. However, since the dielectric constant of the solution rapidly approaches that of the solvent, it is doubtful that the changes shown in Fig. 2 can be due to this effect alone. Unfortunately, no plausible explanation of the pronounced effects of dilution on the carbonyl and C–H bending vibrations can be offered at this time. As mentioned previously, however, the changes in the other spectral lines with dilution are small,[7] and can be attributed, therefore, to changes in the energy difference between two rotational isomers. The following discussion is based on the assumption that rotational isomerism is responsible for most of the observed spectral changes.

Since numerous strong lines present in the spectrum of the liquid are absent in the spectrum of the solid, one can conclude that only one isomeric species is present in the solid. Furthermore, this isomer is the more stable one in the liquid state since the lines due to it increase in intensity as the temperature is lowered. Moreover, this same group of lines decrease in intensity with dilution and hence are due to the more polar form. By similar reasoning, the form which predominates in the gas phase is the less polar form and the less stable or higher energy form in the liquid state.

It would be desirable, of course, to be able to determine the symmetries and energy difference (ΔH) of these two isomers. Considering first the energy difference in the liquid state, one is faced with the problem of finding a pair of lines that are not overlapped. An examination of Fig. 1 shows immediately that the band at 948 cm.$^{-1}$ due to the more stable isomer is the only one in the entire spectrum that meets this specification. Therefore, the best one can do is obtain a lower limit for ΔH, by assuming the bands due to the less stable form do not change with temperature. (Actually they should decrease as the temperature is lowered.) Using the ratio of the intensity of 948 cm.$^{-1}$ at 311 and 400°K., the calculated value of ΔH is 1500 cal./mole.

Many of the strong bands in the infrared spectrum of the liquid and solid due to the more stable isomer (*e.g.*, 732, 815, 948 and 1302 cm.$^{-1}$), are either considerably weaker or absent in the spectrum of the gas. This would indicate that the more stable isomer in the liquid state is on the verge of becoming spectroscopically extinct in the vapor phase. Thus, the less stable form in the liquid state becomes considerably more stable in the gas phase. Mizushima, *et al.*,[1] have observed an almost identical situation in monochloroacetone.

Little can be said at this time with regard to the symmetry of the two isomers. Since the symmetry of all of the conceivable configurations (C_1, C_2, C_s and C_{2v}) is low, the advantages derived from higher symmetry are absent. Consequently, it does not appear possible to determine the specific symmetry of the two isomers by spectroscopic methods only. Moreover, several of the conceivable configurations belong to the same point group even though the orientation of their CH_2Cl end groups is different.

There is one bit of information on the molecular symmetry obtained from X-ray studies on the solid state.[8] X-Ray powder patterns of the two solid forms also show that they are polymorphs. The X-ray patterns are even more distinctly different than the infrared spectra as might be ex-

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(4) K. Kuratani, T. Miyazawa and S. Mizushima, *J. Chem. Phys.*, **21**, 1411 (1953).

(5) A. Wada and Y. Morino, *ibid.*, **22**, 1276 (1954).

(6) S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, New York, N. Y., 1954.

(7) Indeed, the effect was so small for some bands that the trends in intensity escaped detection. In these instances a comparison of the liquid spectrum with a diluted CS_2 solution spectrum was helpful (see Table II).

(8) We are indebted to Dr. R. F. Raeuchle and Mr. F. von Batchelder of the Naval Research Laboratory for providing this X ray data.

pected since all of the possible isomeric forms have all vibrations active in the infrared and Raman spectra. Single crystals of the non-needle-like form could be obtained and preliminary single crystal patterns showed the space group to be C^2/C (C_{2H}^6) or C_c (C_s^4). With these space symmetries the available site symmetries (which will be the same as the molecular symmetry) are C_2 (two-fold axis only) or C_i (center of symmetry) for $C^2/_c$ crystal symmetry and C_1 (no symmetry) for C_c crystal symmetry.

Molecular symmetry can, of course, be higher than C_2 or C_i in the liquid or vapor state, but crystal forces do not require it for the solid state, and probably will, in fact, attempt to eliminate any higher symmetry or planes of symmetry as solidification takes place.

Conclusions

The effects of changes in temperature, state and dilution on the infrared and Raman spectra of dichloroacetone can be reasonably explained on the basis of two rotational isomers. The more polar isomer persists in the solid state and is also of lower energy in the liquid. The lower limit for the energy difference in the liquid was found to be 1500 cal./mole. In the gas phase, the less polar species is much more abundant than the other isomer, indicating a reversal in relative stability in going from liquid to gas.

The molecular symmetries of the two isomers have not been determined due to the similarity of the selection rules for the various conceivable isomers.

WASHINGTON 25, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Infrared Absorption Spectra of Inorganic Coördination Complexes.[1a,b] V. The N-H Stretching Vibration in Coördination Compounds

BY G. F. SVATOS, COLUMBA CURRAN AND J. V. QUAGLIANO

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Coördination with metals by molecules containing H-N bonds results in a marked increase in absorption in the 3 μ region and in a decrease in the frequency of the H-N stretching vibration. The effects of hydration, hydrogen bonding, configuration of the complex and the solvent on the character and position of the absorption peaks in this region have been studied. The shift in the H-N stretching frequency on coördination increases with increasing charge on the complex and with increasing covalent character of the N-M bond. The spectra of salicylaldimine complexes show that the nickel(II) and copper(II) complexes have a *trans* square planar configuration. The N-Ni bond in this complex is revealed to be stronger than the N-Cu bond.

Introduction

Flett[2] has shown that in *para*-substituted anilines delocalization of the unshared pair of nitrogen valence electrons in π-bond formation results in an increase in frequency of the H-N stretching vibration. Both the antisymmetric and symmetric frequencies increase with increasing electron withdrawal of the *para*-substituent, and therefore with increasing double bond character of the nitrogen-to-ring bond. This is not unexpected in the light of the well known increase in frequency of the C-H stretching vibration from ethane to acetylene. In the course of investigation of the infrared spectra of metal coördination compounds in this Laboratory it was observed that the absorption peaks associated with the H-N stretching vibrations of a number of amines shifted to lower frequencies on the formation of nitrogen-to-metal bonds.[3] In this paper are reported the results of a systematic study of this phenomenon. Among the factors investigated were the effects of hydration, hydrogen bonding, configuration of the metal complex, charge on the metal ion and covalent character of the N-M bonds.

Experimental

Preparation and Purification of Compounds.—Bis-(*o*-hydroxyacetophenoneimino)-copper(II) was prepared by a modification of the procedure reported for the preparation of the corresponding nickel complex. Bis-(sarcosino)-zinc(II) dihydrate was prepared in a manner similar to that reported by Dubsky and Rabas[4] for the preparation of the glycine complex. The other compounds listed in Table I were prepared by methods similar to those given in the references listed in the last column of the table. The few compounds in Table II not listed in Table I were supplied by Dr. D. N. Sen.[5] Most of the compounds were dried by heating under reduced pressure in an Abderhalden apparatus for several hours at 110°. Analyses of the compounds are given in Table I.

Absorption Measurements.—Spectra were obtained by means of Perkin-Elmer Infrared Spectrophotometer Model 21, using a calcium fluoride prism. Preparation of the potassium bromide disks were made according to the procedure of Stimson and O'Donnell.[6] Measurements in solution were obtained with 1 cm. quartz cells. The positions and intensities of the absorption maxima of the compounds studied are listed in Tables II and III.

Discussion of Results

A. Intensity of Absorption.—The formation of nitrogen-to-metal bonds by a coördinating group having one or more N-H bonds increases the electron demand of the nitrogen and therefore increases the polarity of the N-H bonds. It is to be expected that the change in the N-H dipole moment during vibration should also increase, resulting in an

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[1] (a) Paper IV in series, THIS JOURNAL, **77**, 5508 (1955). (b) Abstracted from the Ph.D. thesis of G. F. Svatos, Notre Dame, 1954. Presented before the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., Feb., 1954. Supported in part under AEC Contract AT(11-1)-38, Radiation Project of the University of Notre Dame.

[2] M. St. C. Flett, *Trans. Faraday Soc.*, **44**, 767 (1948).

[3] J. V. Quagliano, G. F. Svatos and C. Curran, *Anal. Chem.*, **26**, 429 (1954).

[4] J. V. Dubsky and A. Rabas, *Spisy vydávané přírodovědeckou Fakultou Masarykovy Univ.*, No. 123, 3 (1930); *C. A.*, **25**, 2655 (1931).

[5] D. N. Sen, Ph.D. Thesis, University of Notre Dame, 1954.

[6] M. M. Stimson and M. J. O'Donnell, THIS JOURNAL, **74**, 1805 (1952).