atoms for hydrogen atoms in this series due to a decrease in the ionic character of the chlorine atoms as more chlorine atoms are attached to the same carbon atom. Such a trend is observed for 1,1-dichloroethane, methylchloroform and carbon tetrachloride, the values of the C–Cl distances being 1.795, 1.775 and 1.76 Å., respectively, but an inconsistency occurs in ethyl chloride, where the C–Cl distance is 1.77 Å.

The C–C–Cl and Cl–C–Cl angles (110 ± 4° and 109.5 ± 1.5° respectively) obtained in this investigation are in excellent agreement with results obtained for most of the investigations on other chloroalkanes except *t*-butyl chloride[9,10] and 1,2-dichloropropane,[8] where the C–C–Cl angles are approximately 107 and 108°, respectively. The greatest difference between the results of this investigation and those of other investigations, however, lies in the non-bonded C—Cl distance ($2.74_5 \pm 0.03$ Å.), which is longer than any value reported previously, except for the early value reported by Beach and Stevenson[13] for ethyl chloride (2.74 ± 0.02 Å.).

The large uncertainty on the C–C distance in 1,1-dichloroethane makes it impossible to be certain that this distance is different from the corresponding distance in 1,2-dichloroethane, but it does seem most likely that the latter compound is very unusual in this respect.

[13] J. Y. Beach and D. P. Stevenson, THIS JOURNAL, **61**, 2643 (1939).

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, TOKYO INSTITUTE OF TECHNOLOGY]

The Molecular Structure of α-Chlorocyclohexanone

BY KUNIO KOZIMA AND YOSHIKO YAMANOUCHI

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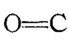
By the measurements of the infrared spectra and the dipole moment of α-chlorocyclohexanone the following results have been obtained that the molecules of α-chlorocyclohexanone in the vapor or the liquid state are in a dynamic equilibrium of mutually convertible isomers represented by the usual symbols as follows (e) ⇄ (a) and that the (e)-form is more stable in the liquid state and only this form persists in the solid state. The energy difference between the isomers was approximately determined. Variation of the energy difference with solvents can be estimated by use of the reaction field theory of Onsager.

It has been well established that the ring structure of various cyclohexane derivatives is the chair form. Because the valency angle of  $O{=}C\langle^{C}_{C}$ of cyclohexanone should be about 120°, its ring structure may be somewhat different from that of usual cylcohexane derivatives. It seems reasonable, however, that the ring structure is nearly the chair form. We can expect, therefore, that the molecules of α-chlorocyclohexanone in the vapor or the liquid state are in a dynamic equilibrium of the two mutually convertible isomers (inverted isomers)[1] represented by the usual symbols[2] as

$$(e) \rightleftarrows (a)$$

where e and a represent the position of chlorine atom attached to the ring, respectively. Both forms are shown schematically in Fig. 1.

In an earlier paper[3] it was described that most of the molecules of α-chlorocyclohexanone in the liquid exist as the axial form, although a small amount of the equatorial form probably exists.

This work was undertaken with the primary purpose of determining the energy difference between the two isomers, special interest being centered in the determination of the more stable form of this compound.

α-Chlorocyclohexanone was prepared by the method of Bartlett and Rosenwald[4] and had b.p. 71.5–72.5° at 6 mm., m.p. 23.0°.

The measurements of infrared absorption spectra were made with a Perkin–Elmer 112 spectrometer. NaCl and KBr prisms were employed to cover 2 to 25 μ. A CaF_2 prism was used to study the band shape of the C=O stretching vibrations.

The Raman spectrograph and other apparatus used in this work have been described previously.[1a]

The wave number readings of the Raman bands and the infrared absorption maxima are listed in Table I. The intensities are shown by the usual symbols, respectively. Carbon disulfide was used for obtaining the spectra in non-polar solvent. Because of the overlap of the absorption of carbon disulfide and that of the solute, the bands at 1438 and 1450 cm.$^{-1}$ for non-polar solvents were obtained in carbon tetrachloride.

In order to determine the energy difference between the two isomers, the temperature dependence of the relative intensities of the two bands at 917 and 933 cm.$^{-1}$ which are due to the different forms of the compound was measured for the CS_2 dilute solution and for the pure liquid. The true integrated absorption intensities A corrected for finite slit widths were calculated from the equation

$$A = K(1/CL)\log_e(T_0/T)_{\nu(\max)} \times \Delta\nu^{a}_{1/2}$$

where the letters have their usual meanings. The values of K were obtained from the table of Ramsay.[5] The results obtained are shown in Table II.

The dipole moment was measured by the usual solution method. The results are shown in Table III.

Discussion of Results

As is clear in Table I, the infrared bands of the liquid spectra are divided into two groups, ac-

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[1] (a) K. Kozima and T. Yoshino, THIS JOURNAL, **75**, 166 (1953); (b) K. Kozima, K. Sakashita and S. Maeda, *ibid.*, **76**, 1965 (1954).

[2] D. H. R. Barton, O. Hassel, K. S. Pitzer and V. Prelog, *Nature*, **172**, 1096 (1953); *Science*, **119**, 49 (1953).

[3] E. J. Corey, THIS JOURNAL, **75**, 2301 (1953).

[4] P. D. Bartlett and R. H. Rosenwald, *ibid.*, **56**, 1992 (1934).

[5] D. A. Ramsay, *ibid.*, **74**, 72 (1952).

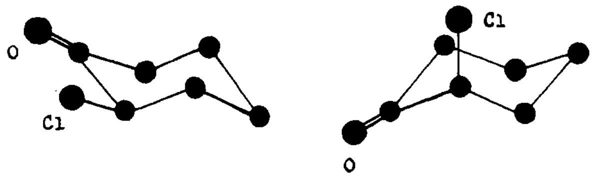
TABLE I

VIBRATION SPECTRA OF α-CHLOROCYCLOHEXANONE[a]

Raman spectra, cm.$^{-1}$ Liquid	Infrared spectra, cm.$^{-1}$ Vapor	CS$_2$ soln. (CCl$_4$ soln.)	Liquid	Solid	Configurations
421(2)	444(w)	444(m)	445(m)	....	a
	471				
486(6)	476(w)	477(m)	479(s)	489(m)	e
	484				
	538(s)	534(s)	535(vs)	....	a
538(10br)	542(m)	543(s)	541(vs)	541(s)	e
663(4)		656(w)	661(m)	661(m)	e
	697(m)				
698(4)	705(s)	700(m)	699(m)	....	a
716(4)	712(m)	713(m)	714(s)	711(s)	e
752(3)	754(wbr)	754(m)	753(m)	....	a
796(3)	798(m)	799(s)	798(vs)	798(s)	e
	818(w)	822(m)	823(m)	....	a
832(5br)	825(m)	....	830(w)	833(m)	e
	833(w)				
	840(w)	838(w)	839(vw)	....	a
855(4)	....	....	853(w)	853(m)	e
896(4)	891(w)	891(w)	892(m)	891(m)	e
919(1)	910(w)				
	918(m)	915(m)	917(m)	....	a
	925(w)				
928(4)		932(w)	934(m)	934(s)	e
969(6)		969(m)	968(s)	970(s)	e
	974(m)				
	982(m)	980(m)	980(sh)	....	a
	991(w)				
1019(6)	1020(w)	1022(m)	1027(m)	1028(m)	e
1065(6)	1065(mbr)	1060(s)	1063(m)	1065(m)	e
1098(1)	....	1096(w)	1098(w)	1098(w)	e
	1110(m)				
1121(4)	1117(s)	1116(m)	1119(m)	1121(s)	e
	1125(m)				
1192(4)	1193(m)	1191(w)	1194(m)	1194(m)	e
	....	1207(w)	1208(w)	....	
	1227(sbr)	1224(m)	1226(m)	1229(vw)	
1250(6)	1263(m)	1258(m)	1258(m)	1261(m)	
	1296(m)	1295(m)	1298(m)	....	
1308(6)	1307(mbr)	1309(m)	1307(m)	1310(s)	
1332(2)	1317(w)	1338(w)	1334(w)	1331(w)	
	1350(w)	1345(w)	1349(w)	....	
1425(2)	1438(m)	1438(m)	1430(s)	1428(s)	
1447(8)	1451(m)	1450(s)	1445(s)	1456(m)	
1721(5)	1739(vsbr)	1723(vsbr)	1723(vsbr)	1723(vsbr)	
		1745(vwsh)	1743(vwsh)	1743((vvwsh)	
2899(8)	2861(m)	2869(m)	2866(m)	2869(m)	
2949(10)	2935(s)	2949(s)	2930(s)	2944(s)	
	3406(vw)	3420(vw)	3401(w)	3396(w)	

[a] w = weak, m = medium, s = strong, v = very, br = broad and sh = shoulder.

cording to whether or not the bands persist in the spectra of the solid. As are the cases for *trans*-1,2- and *trans*-1,4-dihalocyclohexanes,[1] this behavior can be explained if one group of the bands is due to one and the other group is due to the other of the two isomers, (a) and (e), of the compound.



(e)-form (a)-form

Fig. 1.—Two forms of α-chlorocyclohexanone.

It seemed to be of considerable interest to determine which of the two mutually convertible isomers predominates in the liquid and exists exclusively in the solid. To answer the problem, let us consider again the results shown in Table I.

As is seen easily from Table I, the relative intensities of the bands which persist in the solid become stronger in the pure liquid than in the vapor and in the solution of non-polar solvent. It is generally true that the more polar of two interchangeable forms becomes more stable in a solvent of higher dielectric constant, except in the

TABLE II

TEMPERATURE DEPENDENCE OF THE RELATIVE INTENSITIES

Temp., °C.	Wave no.	Form	Log$_e$ (T_0/T)	$\Delta\nu^{a}{}_{1/2}$	K	A_aC_a/A_eC_e
(1) CS$_2$ solution (0.37 mole/l.)						
24	915	a	1.00	4.8	1.53	2.6
	932	e	0.232	8.0	1.54	
−24	915	a	1.18	3.7	1.54	2.0
	932	e	0.346	6.4	1.52	
				ΔE obtd. 0.81 kcal./mole		
(2) Pure liquid						
75	917	a	0.369	6.7	1.53	1.2
	934	e	.210	10.0	1.55	
25	917	a	.528	5.7	1.55	0.89
	934	e	.369	9.2	1.55	
				ΔE obtd. 1.1 kcal./mole		
(3) Pyridine solution (0.85 mole/l.)						
25	915	a	0.917	6.1	1.53	1.2
	932	e	0.576	8.2	1.53	
				ΔE obtd. 0.94 kcal./mole		

TABLE III

DIPOLE MOMENT OF α-CHLOROCYCLOHEXANONE

Molar fraction	Density	Dielectric constant	P_{12}	P_2
Solvent, CCl$_4$, temp., 27°				
0.0000	1.5805	2.2235	28.197	
.003239	1.5792	2.2705	28.969	267
.005281	1.5780	2.3037	29.511	277
.005715	1.5779	2.3091	29.596	273
			$P_{2\infty}$ (mean)	272

$R_D = 32.6$ $P_0 = 239$ dipole moment $\mu = 3.43\,D^{a}$

[a] When the dipole moment was calculated using the method of Halverstadt and Kumler (THIS JOURNAL, **64**, 2988 (1942)), the value of the orientation polarization P_0 was 244 cc. and that of μ was 3.46 D.

case of benzene.[6] One can therefore attribute the bands which persist in the solid to the more polar (e)-form and the other bands to the less polar (a)-form.

The fact that the bands of the (e)-form in the liquid spectra are generally stronger than the other bands leads us to the conclusion that the (e)-form also predominates in the liquid state. As this conclusion, however, is quite contrary to Corey's interpretation,[3] we proceeded to obtain further evidences.

The temperature dependence of the integrated intensity of the band at 917 cm.$^{-1}$ of the (a)-form and that at 933 cm.$^{-1}$ of the (e)-form were measured. Though the bands selected are different in the values of the molecular extinction coefficients, the band shapes are adequate for our purpose.

As shown in Table II, the relative intensities of the band at 917 cm.$^{-1}$ to that at 937 cm.$^{-1}$ increase with rising temperature. In agreement with our foregoing statement we can conclude that the (e)-form is more stable than the (a)-form in the liquid or in the solution. From these data we can calculate as usual the difference ΔE between the energy E_a of the (a)-form and the energy E_e of the (e)-form ($\Delta E = E_a - E_e$) by the equation

$$C_aA_a/C_eA_e = (\alpha_a f_a/\alpha_e f_e)\exp(-\Delta E/RT)$$

where A_a and A_e are the true integrated absorption intensities of the bands at 917 and 933 cm.$^{-1}$, C_a and C_e the concentrations (mole/l.), α_a and α_e the molecular absorption coefficients, and f_a and f_e the partition functions of each of the structures shown by the suffixes, respectively. In order to eliminate the unknown quantity $(\alpha_a f_a/\alpha_e f_e)$, the measurements were made at two temperatures. The ratio of the partition functions, f_a/f_e, is taken to be constant, because of the narrow range of temperature. The values obtained for ΔE are 1.1 kcal./mole in the pure liquid and 0.81 kcal./mole in the carbon disulfide solution. The (e)-form becomes about 0.3 kcal./mole more stable in the pure liquid than in the dilute non-polar solution.

The ratio $\alpha_a f_a/\alpha_e f_e$ for the liquid was estimated to be 5.8. From the data shown in Table II and based on the assumption that this ratio does not appreciably change in the case of the pyridine solution, the value of ΔE in this solution can be obtained as 0.94 kcal./mole.

The value of ΔE in the vapor also was measured. Since the rotational structures of the bands appeared in this case, the area intensities were obtained by the graphical integration. Since such a high temperature, at which the measurements were made, causes emission bands of the compound with noticeable intensities, various precautions must be taken for the measurements and for the evaluation of absorbances. The procedure for the measurements is the same as described in our previous paper.[7] As shown in Table IV, the ratio of the relative intensity of the band near 754 cm.$^{-1}$ of the (a)-form to that near 798 cm.$^{-1}$ of the (e)-form is almost independent of the temperature. The fact indicates that the value ΔE in the vapor is nearly zero.

TABLE IV

TEMPERATURE DEPENDENCE OF THE RELATIVE INTENSITY FOR THE VAPOR

Temp., °C.	Wave no.	Form	Band area (by weighing), g.	Ratio of the band area
180	754	a	0.0630	0.425
	798	e	.1484	
110	754	a	.0498	0.428
	798	e	.1163	
		ΔE obtd. 0.0 kcal./mole		

Based on the reaction field theory of Onsager,[8] it is well known[9] that the more polar (e)-form becomes more stable by an amount of energy $\Delta(\Delta E)$ than the less polar (a)-form, when the molecules are transferred from the vapor to a medium of dielectric constant ϵ, and the change of energy difference is

$$\Delta(\Delta E) = \frac{(\epsilon - 1)}{(2\epsilon + 1)a^3}(\mu_e^2 - \mu_a^2)$$

where μ_e and μ_a are the dipole moments of the forms shown by the suffixes, respectively, and a^3 is the molecular volume. Upon the basis of simple vector addition, the value of the moment μ_e is estimated to be 3.6 D by taking account of the

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(6) S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, Inc., New York, N. Y., 1954, p. 43.

(7) K. Kozima and K. Sakashita, *Bull. Chem. Soc. Japan*, **31**, 796 (1958).

(8) L. Onsager, THIS JOURNAL, **58**, 1486 (1936).

(9) See ref. 6, p. 42.

inductive effect between the bond moment of C=O and that of C–Cl and assuming that these bonds are in the same plane for this form.[10] This value is the same as that estimated by Mizushima, *et al.*,[11] for the more stable rotational isomer of α-chloroacetone. The moment μ_a is similarly estimated to be 2.5 D which is nearly the same as that estimated by Kumler, *et al.*,[12] for the (a)-form. The value of a^3 was determined to be 4.54 $\times 10^{-23}$ cc. by the measurement of density at 23° ($d^{23}{}_4$ 1.158). The dielectric constant of this substance was measured to be 26.8 at the same temperature. By use of these values the values of $\Delta(\Delta E)$ were calculated. The results are shown in Table V together with the energy differences determined by the intensity measurements. The value of $\Delta(\Delta E)$ and those of ΔE have the same meaning, because the energy difference ΔE in the vapor is nearly zero.

TABLE V

ENERGY DIFFERENCE BETWEEN THE TWO FORMS

State	Dielectric constant	ΔE, kcal./mole Obsd.	ΔE, kcal./mole Calcd.
Pure liq.	26.8	1.11	1.0
Pyridine soln.	12.5	0.94	0.94
CS_2 soln.	2.63	0.81	0.55

The contour of the broad band near 1730 cm.$^{-1}$ was investigated for the various states by use of the CaF_2 prism. Because of a complicated feature of the contour, it seems difficult to divide the broad band into the band of the (e)-form and that of the (a)-form.

The band at 714 cm.$^{-1}$ may be assigned to the C–Cl stretching vibration for the (e)-form and the band at 699 cm.$^{-1}$ to that for the (a)-form. The assignments are in agreement with the rule[13] reported by one of the authors that for the C–X (X = halogen) stretching frequencies of various cyclohexane derivatives the frequency of the C–X bond having the X atom in the (e)-orientation is higher than that of the bond having the X atom in the (a)-orientation. According to Jones, *et al.*,[14] the band at 1430 cm.$^{-1}$ may be assigned to the scissoring vibration of the α-methylene group next to the carbonyl group.

By use of the moments, μ_e and μ_a, estimated for the two isomers and of the energy difference ΔE determined by the intensity measurements the dipole moment μ can be calculated by the formula

$$\mu = \{(r\mu_a^2 + \mu_e^2)/(1 + r)\}^{1/2}$$

where r is the abundance ratio of two isomers and is given approximately as

$$r = \exp(-\Delta E/RT)$$

The calculated value of 2.3 D is in good agreement with the observed value listed in Table III. In agreement with the results obtained by studying the infrared spectra, the observed value of the dipole moment also is evaluated by considering only the equilibrium of the (e)- and the (a)-form without assuming the coexistence of any other form, such as a flexible form assumed by Kumler, *et al.*[12]

[10] This assumption seems to be reasonable when taking account of the structure of α-methylcyclohexanone determined by C. Romers (*Rec. trav. chim.*, **75**, 956 (1956)) with the aid of electron diffraction.

[11] S. Mizushima, T. Shimanouchi, T. Miyazawa, I. Ichishima, K. Kuratani, I. Nakagawa and N. Shido, *J. Chem. Phys.*, **21**, 815 (1953).

[12] W. D. Kumler and A. C. Huitric, THIS JOURNAL, **78**, 3369 (1956).

[13] K. Kozima, *Bull. Tokyo Inst. Tech.*, 1 (1952) (in Japanese).

[14] R. N. Jones and A. R. H. Cole, THIS JOURNAL, **74**, 5648 (1952).

O-OKAYAMA, MEGURO-KU, TOKYO, JAPAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, KANSAS STATE UNIVERSITY OF AGRICULTURE AND APPLIED SCIENCE]

Neutron and γ-Irradiation of Phosphorus Trichloride[1]

BY D. W. SETSER, H. C. MOSER AND R. E. HEIN

RECEIVED AUGUST 11, 1958

Samples of liquid phosphorus trichloride were reactor irradiated for varying lengths of time, and the yield of P^{32}-labeled PCl_3 was measured. The percentage of the P^{32} in combination as $P^{32}Cl_3$ changed from 60 to 90% with increasing irradiation time. A radiation induced oxidation of radioactive P_2Cl_4 to form PCl_3 has been postulated to explain the changing distribution of P^{32}. Two labeled products, $P^{32}OCl_3$ and $P^{32}Cl_3$, were identified in reactor irradiated $POCl_3$. The relative yield of $P^{32}OCl_3$ was also found to increase with irradiation time.

Introduction

The present study was undertaken to investigate the chemical effects accompanying $P^{31}(n,\gamma)P^{32}$ reactions in PCl_3 and to determine what influence the γ-ray dosage has upon the distribution of products containing P^{32}. When samples of PCl_3 are reactor irradiated, they are subjected to a large γ-ray flux because of contributions from both external and internal sources. This system is also somewhat unusual in that recoil atoms from nuclear reactions should thermalize rapidly because all of the atoms have nearly equal mass.

Phosphorus atoms of PCl_3 which capture neutrons are very likely given enough recoil energy to break one or more of their bonds. The initial γ-ray emitted by a phosphorus atom following neutron capture is 3.5 Mev. or greater[2] which produces a recoil energy of at least 205 e.v. This is sufficient energy to break the chemical bonds in PCl_3 (3.4 e.v.) unless successive emission of γ-rays cancels the recoil energy.

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[1] Work performed under contract No. AT (11-1)-584 with the U. S. Atomic Energy Commission. Taken in part from a thesis submitted by Donald W. Setser in partial fulfillment of the requirements for the degree of Master of Science, January, 1958.

[2] B. B. Kinsey, G. A. Bartholomew and W. H. Walker, *Phys. Rev.*, **85**, 1012 (1952).