sulting solution was acidified and the phosphorous acid was oxidized to phosphoric by evaporating the solution almost to dryness with aqua regia. The precipitation of the ammonium phosphomolybdate was carried out in the usual manner. Considering the precision of the methods for determining phosphorus in compounds of this type, the result, 29.87% P, is in good agreement with the formulation F_3PBH_3 (30.43% P).

5. **Measurement of Physical Properties of H_3BPF_3.**—Conventional techniques were used for vapor density and vapor pressure measurements. Temperatures were measured with ethylene and carbon dioxide vapor pressure thermometers. The melting point was obtained in the vacuum line using the method of Stock.[11]

6. **Reaction of F_3PBH_3 with Trimethylamine.**—One and ninety three hundredths mmoles of F_3PBH_3 was condensed in a 250-ml. bulb with 2.31 mmoles of trimethylamine. When the mixture was warmed to room temperature there was an immediate reaction in which a white solid was produced. The bulb was cooled to −80°, the more volatile products were distilled out, the bulb was weighed, the trimethylamine–borane was sublimed out, and the bulb was reweighed. A 97% yield (0.1362 g.) of $(CH_3)_3NBH_3$ was obtained. Vacuum line distillation of the volatile gases yielded 79.3% of the theoretical PF_3. This was characterized by vapor pressure and molecular weight measurements (obsd. 87.6; theory 87.98). The unrecovered PF_3 (0.4 mmoles) corresponded exactly to the excess of trimethylamine (0.38 mmole), a fact which suggests that a reaction between PF_3 and $N(CH_3)_3$ had taken place to yield the unidentified solid and gaseous products. This postulate was checked by allowing a small amount of trimethylamine to react with an excess of PF_3. An approximately one to one reaction occurred to produce a non-volatile white solid and a mixture of gaseous products which were qualitatively the same as those observed previously.

7. **Reaction of F_3PBH_3 with Ammonia.**—A quantity of dry ammonia, 14.70 mmoles, was condensed on the walls of the reaction tube. Then, 2.20 mmoles of F_3PBH_3 was added and the temperature was raised from −128 to −80° over the period of 2.5 hours. The excess ammonia was then sublimed from the reaction tube at −80°. The amount of ammonia recovered was 3.69 mmoles, meaning that 5.0 moles of ammonia react with one mole of F_3PBH_3.

The reaction product was a white solid which began to decompose at room temperature by turning yellow and giving off small amounts of hydrogen. Upon heating the solid to about 55° an amount of ammonia equivalent to 1.62 moles of the original 5.0 was recovered. During the decomposition a small amount of a white solid of very low vapor pressure was collected in a Dry Ice trap. This white solid burst into flames when the trap was cleaned with concentrated nitric acid.

8. **Preparation of Nitrogen Trifluoride.**—Nitrogen trifluoride was prepared by a modification of the method of Ruff.[12] A closed electrolysis cell was substituted for Ruff's open cell.

The impure NF_3 was bubbled slowly through a warm KI solution. Final purification was achieved by low temperature fractionation in the vacuum line. The gas was passed slowly through a trap cooled to −183° with liquid oxygen. The impurities, principally small amounts of N_2O, condensed, while the NF_3 passed through into a third trap cooled to −208° with low pressure liquid nitrogen (maintained at 100 mm. pressure by pumping through a manostat). Small amounts of dissolved oxygen and nitrogen were pumped from the NF_3 in the third trap to give a product of high purity. The molecular weight of the gas, as determined by vapor density, was 71.2. The theoretical value for NF_3 is 71.01.

9. **The Reaction of Nitrogen Trifluoride with Diboranes.**—The sealed tube high pressure techniques described for the preparation of F_3PBH_3 were employed. In a typical run 2.61 mmoles B_2H_6 and 18.84 mmoles NF_3 were sealed into a bomb tube and allowed to stand for 8 days at room temperature. When the tube was opened to the line, the amount of non-condensable gas was negligible. A mixed pentane bath at −155° was placed around the tube, and the entire contents distilled into the vacuum system. On further fractionation in the vacuum line no fraction could be retained in the −155° trap. Finally, during a transfer distillation a violent explosion occurred. The temperature of the vessel at the time of the explosion was estimated to be about −170°, since a liquid nitrogen Dewar had just been removed and another low temperature bath was to be substituted. The explosion occurred before the second bath was put in place. In a second trial under similar circumstances an explosion occurred while the contents of the reaction tube were being distilled into the vacuum line.

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(11) A. Stock, *Ber.*, **50**, 156 (1917).

(12) O. Ruff, J. Fischer and F. Luft, *Z. anorg. Chem.*, **172**, 417 (1928).

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

The Ultraviolet Absorption Spectrum of Oxalyl Chloride Vapor; Spectral Evidence for Rotational Isomerism[1]

BY JEROME W. SIDMAN[2]

RECEIVED OCTOBER 27, 1955

The long wave length ultraviolet absorption spectrum of oxalyl chloride has been studied in the vapor phase at temperatures between 25 and 275°. From the temperature dependence of the spectrum, it is concluded that the spectrum is due to two isomeric forms. The *trans*-form shows sharp structure, for which a partial vibrational analysis is presented, whereas the absorption attributed to the *cis*-form appears to be continuous. The results are discussed with reference to the vibrational spectra of oxalyl chloride. The structure of $(ClCO)_2$ is also compared with the structure of the related molecules, $(CHO)_2$ and $(CH_3CO)_2$.

Introduction

Although oxalyl chloride, $(ClCO)_2$, has been the subject of several spectroscopic investigations, a survey of the literature reveals the absence of agreement concerning the existence of rotational isomers of this molecule. Ziomek, Meister, Cleveland and Decker[3] (henceforth called ZMCD) have studied the Raman and infrared spectra of oxalyl chloride, and have performed force constant calculations for both the *cis*- and *trans*-forms. ZMCD conclude that a satisfactory assignment of the Raman and infrared bands can be made by assuming oxalyl chloride to exist in the *trans*-form alone.

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(1) This research was supported by the Office of Ordnance Research under Contract DA-30-115-Ord-620 with the University of Rochester.

(2) Shell Post-Doctoral Fellow, 1955–1956.

(3) J. S. Ziomek, A. G. Meister, F. F. Cleveland and C. E. Decker, *J. Chem. Phys.*, **21**, 90 (1953).

Table I

Vibrational Analysis of the Absorption Spectrum of $(ClCO)_2$ Vapor

7-cm. cell, 22°, approximate errors: 26500–28000, ± 2 cm.$^{-1}$; 28000–29500, ± 5 cm.$^{-1}$; 29500–31000, ± 10 cm.$^{-1}$; 31000–32500, ± 20 cm.$^{-1}$; 32500–34000. ± 30 cm.$^{-1}$.

Intensity	ν, cm.$^{-1}$	Assignment	Intensity	ν, cm.$^{-1}$	Assignment	Intensity	ν, cm.$^{-1}$	Assignment
vvw	25973		w	27827		w	29323	
vvw	26549		w	27857		w	29381	
w	26585		w	27871		w	29403	
w	26600	I − 501–85	w	27895		w	29542	
vw	26632		w	27930		w	29578	III − 501?
vw	26643		w	27944		m	29595	
m	26680, 26695	I − 501	w	27986		w	29663	
w	26757, 26770	I − 501 + 77	w	28019		w	29704	
vw	26806		w	28052		w	29730	
vw	26847		w	28075	II − 501 − 85	w	29800	
vw	26891		w	28095		m	29889	
vw	26966		w	29115		m	29970	
vw	27010		m	28149, 28169	II − 501	w	29986	III − 85
m	27091	I − 501 + 397	w	28191		s	30029	
s	27104	I − 85	w	28234	II − 501 + 77	ms, vs	30066, 30085	III
m	27142		w	28265		vs	30155	III + 77
m	27165		w	28305		m	30236	
m	27177		mw	28339		w	30271	
vs	27189 (red edge)	I	mw	28370		m	30352	
m	27157		mw	28408		mw	30423	
m	27163		m	28438		w	30481	III + 397?
s	27266	I + 77	mw	28467		w	30539	
m	27275		ms	28507		w	30625	
w	27298		mw	28536		w	30701	
vw	27346		mw	28577	II − 85	w	30798	
w	27388		vs	28601		w	30877	
w	27401		vvs	28645, 28659	II	w	30959	
m	27469		s	28723, 28740	II + 77	w	31015	
w	27499	I + 397 − 85	w	28777		w	31140	
m	27546		w	28819		m	31445	
w	27575		mw	28855		s	31495	IV
s	27586 (red edge)	I + 397	mw	28889		s	31570	IV + 77
w	27620		s	28920, 28941		s	31635	
ms	27662	I + 397 + 77	s	29005		ms	31765	
w	27688		s	29042, 29069	II + 397	vs	32910	
w	27731		m	29123	II + 397 + 77	vs	32960	
w	27748		m	29203		ms	34260	V
w	27789		m	29267				

However, Saksena and Kagarise[4] (henceforth called SK) have studied the temperature dependence of the Raman and infrared spectra. From the observed temperature dependence they concluded that some of the observed bands are due to the *cis*-form. Kagarise[5] has compared the infrared absorption spectra of oxalyl chloride in the liquid and solid states. The absence in the solid of several bands which are prominent in the liquid appears to provide evidence for rotational isomerism in oxalyl chloride.

Although the ultraviolet absorption spectrum of oxalyl chloride vapor has been measured by Saksena and Kagarise,[6] the dispersion used in their measurements was too low to permit an accurate vibrational analysis of the absorption spectrum. It was felt that a more accurate measurement of the ultraviolet spectrum, combined with a temperature-dependence study, might be of assistance in elucidating the structure of this molecule.

The absorption, fluorescence and phosphorescence spectra of the related molecules, glyoxal[7] $(CHO)_2$, and biacetyl[8] $(CH_3CO)_2$, have been studied recently. A study of the spectrum of $(ClCO)_2$ should therefore be of interest in comparing the electronic and molecular structure of these molecules, and in helping to understand their photochemical properties.

Experimental

The spectrograph used in this research was a Bausch and Lomb quartz prism Littrow instrument. The reciprocal linear dispersion is approximately 8 Å./mm. at 3650 Å. The spectra were recorded on Kodak 103-0 plates, using a tungsten strip filament lamp as a light source. Iron arc calibration spectra were recorded on the same plate by using a Hartmann diaphragm, thereby avoiding any movement of the plate between exposures. The slit width was 15 microns. Under these experimental conditions, the lines of the iron arc at 3099.901, 3100.309 and 3100.671 Å. were easily resolved. The plate readings were converted to

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[4] B. D. Saksena and R. E. Kagarise, *J. Chem. Phys.*, **19**, 987 (1951).

[5] R. E. Kagarise, *ibid.*, **21**, 1615 (1953).

[6] B. D. Saksena and R. E. Kagarise, *ibid.*, **19**, 999 (1951).

[7] J. C. D. Brand, *Trans. Faraday Soc.*, **50**, 431 (1954).

[8] J. W. Sidman and D. S. McClure, This Journal, **77**, 6461, 6471 (1955).

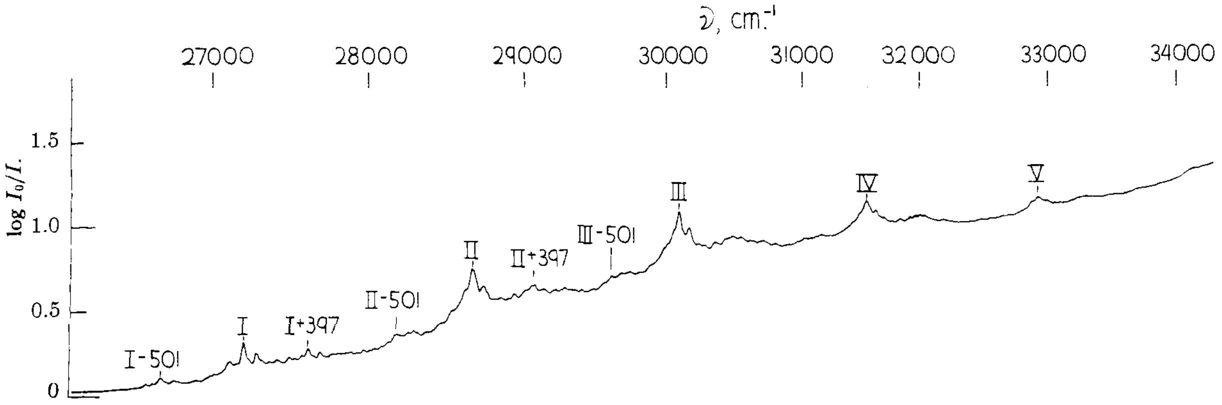

Fig. 1.—Absorption spectrum of $(ClCO)_2$; vapor phase, 7 cm. cell, 22°, Cary double beam recording spectrophotometer, slit width 20 to 35 μ.

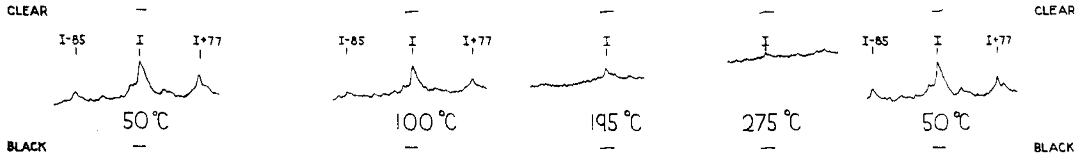

Fig. 2.—Temperature dependence of the absorption spectrum of $(ClCO)_2$, microphotometer tracing of a plate obtained with the Littrow spectrograph. Slit width 15 μ, 103–0 plate. Each exposure is 30.0 sec.

wave lengths by use of a Hartmann dispersion formula which reproduced the wave lengths of the iron arc calibration spectra to 0.1 Å. The wave lengths were then converted to wave numbers *in vacuo* (cm.$^{-1}$).

Eastman Kodak oxalyl chloride (white label grade) was purified by vacuum distillation in an all glass vacuum line containing no stopcocks or stopcock grease. Samples were then vacuum distilled into the small sidearm of a 7-cm. quartz absorption cell fitted with a quartz–Pyrex seal on the sidearm. The sample was frozen under liquid nitrogen and the cell was then sealed off under vacuum and removed from the vacuum line. In this manner, it was possible to purify the oxalyl chloride and to transfer it into the cell in the absence of air or stopcock grease. These precautions were taken since oxalyl chloride reacts with water and stopcock grease.

An insulated nichrome heater was wound around the cell, and a separate heating coil was wound around the sidearm. Temperatures were controlled by separate Variacs for the sidearm and cell, and were measured with a chromel–alumel thermocouple.

A satisfactory absorption spectrum could be recorded with the 7-cm. cell and sidearm at room temperature. In studying the temperature dependence of the spectrum, there was no liquid in the cell or sidearm, and the temperature of the sidearm was maintained slightly higher than the temperature of the cell. This ensured that the number of molecules in the optical path was constant at all temperatures.

Absorption spectra were also recorded on the Cary double beam recording spectrophotometer. However, all wave length measurements were made from the best plates taken with the Littrow spectrograph.

Results and Discussion

a. Vibrational Analysis of the Absorption Spectrum.—The absorption bands which are observed in a 7-cm. path length of oxalyl chloride vapor which is in equilibrium with the liquid at 22° are listed in Table I. A Cary spectrophotometer tracing is shown in Fig. 1. The tracing does not show all of the fine structure which can be observed at the low frequency end of the spectrum. A microphotometer tracing of the band at 27189 cm.$^{-1}$ is shown in Fig. 2. The microphotometer tracing was recorded from a plate obtained with the Littrow spectrograph.

Although the spectrum consists of many bands, several features are very prominent and thus simplify the analysis. The Cary tracing shows that the absorption is due to sharp structure which is superimposed on a continuum. The sharp structure becomes increasingly broad at higher frequencies, and the continuum obscures the sharp structure above 33000 cm.$^{-1}$. The very sharp band at 27189 cm.$^{-1}$ which is shaded to the violet is the most prominent band in the low frequency end of the spectrum. A reasonable vibrational analysis can be performed if this band is chosen as the origin of the analysis. The most prominent feature of the spectrum is the progression of a vibrational frequency of 1420–1460 cm.$^{-1}$ in the upper state. Four members of this progression can be seen before the structure is obscured by the continuum. The intervals between successive members of the main progression I, II, III, IV, V are 1463, 1423, 1420 and 1413 cm.$^{-1}$. The second difference is not constant, and it is difficult to account in detail for the observed variation in the main interval. Part of the variation may be due to perturbation of the vibrational levels of the excited state by other neighboring electronic states of the molecule.

The bands I and II are actually doublets, as is seen in Table I. The doublet splitting in is 14 cm.$^{-1}$ in I and 19 cm.$^{-1}$ in II. Bands III, IV and V are too broad to resolve this splitting, which is possibly due to Fermi resonance in the upper state, although the analysis is too incomplete to allow any definite assignment of the perturbing vibrational levels.

An upper state vibrational frequency of 397 cm.$^{-1}$ is prominent in combination with many of the bands of the main progression. The corresponding frequency in the ground state also appears in the spectrum as a doublet, -494 and -509 cm.$^{-1}$, which combines with bands I, II and III.

The experimental results of Saksena and Kagarise[6] are in fair agreement with these measurements, considering the lower dispersion of SK's spectrograph, but the analysis of the spectrum is not the same. SK find a progression of 949 cm.$^{-1}$, which is assigned in this work as the combination of the bands of the main progression I, II, III, IV, V, with -501 cm.$^{-1}$. The progression of 1384 cm.$^{-1}$ reported by SK is assigned in this work to a combination of the bands of the main progression with the difference frequency of -85 cm.$^{-1}$, which is fairly prominent in the tracings seen in Figs. 1 and 2. The 77 cm.$^{-1}$ difference frequency is also prominent in combination with the bands of the main progression.

The main features of the spectrum are thus explained if 27189 cm.$^{-1}$ is chosen as the origin of the analysis. The ground state vibrational frequency 501 cm.$^{-1}$ (average) and the excited state vibrational frequencies 397 cm.$^{-1}$ and 1420 to 1460 cm.$^{-1}$ plus the difference frequencies 77 and -85 cm.$^{-1}$, can be combined to give a fair analysis of most of the prominent features of the spectrum. Other vibrational frequencies may be hidden in the numerous bands of the spectrum.

b. **Temperature Dependence of the Absorption Spectrum.**—In order to seek possible evidence for the existence of rotational isomers of $(ClCO)_2$, the temperature of the gas was varied without altering the total number of molecules in the optical path. The effect of temperature on the spectrum is quite marked. As the temperature is increased from 50 to 275°, it is found that the intensity of the sharp structure decreases, becoming almost undetectable at 275°, whereas the intensity of the continuum increases. This is seen in the microphotometer tracing in Fig. 2, where the spectrum is shown in the vicinity of 27189 cm.$^{-1}$. The behavior of the remainder of the spectrum is identical. The phenomenon is completely reversible, showing that no permanent change has occurred upon heating to 275° for five minutes.[9]

c. **Assignment of the Electronic Transitions.**—Since the sharp structure decreases in intensity as the temperature is raised, whereas the continuous absorption simultaneously increases in intensity, it appears reasonable to assign the sharp structure and the continuum to electronic transitions belonging to separate molecular species. SK have found a reversible temperature dependence of the bands in the Raman spectrum,[4] and have attributed this to a reversible equilibrium between *cis* and *trans* rotational isomers of oxalyl chloride. As the temperature is increased, the Raman bands assigned to the *cis*-form increase in intensity, whereas the bands assigned to the *trans*-form show a decrease in intensity. Consequently, it appears necessary to assign the continuous background observed in the ultraviolet absorption spectrum to the *cis*-form, while the superimposed sharp structure is assigned to the *trans*-form.

The low intensity of this transition favors an assignment of the $n-\pi^*$ type.[10] The LCAO-MO's for molecules containing the XCOCOX chromophoric group have been previously discussed.[8] If the effect of the Cl atoms in $(ClCO)_2$ is treated as a relatively small perturbation on the –COCO– chromophore, the electronic structure of $(ClCO)_2$ should not differ too greatly from that of $(HCO)_2$ or $(CH_3CO)_2$. The first excited $n-\pi^*$ configuration of the *trans*-form gives rise to four excited states, I^3A_u, I^3B_g, I^1A_u, and I^1B_g, whereas the corresponding states in the *cis*-form are I^3A_2, I^3B_1, I^1A_2 and I^1B_1. The ground state of each form arising from the lowest configuration is ^1A_g for the *trans* and $^1A_1$ for the *cis*. In glyoxal, a rotational analysis of the absorption spectrum has shown that the strongest transition in the visible region is the $I^1A_u \leftarrow {}^1A_g$ transition,[6] and the $I^3A_u \leftarrow {}^1A_g$ transition has also been located. In biacetyl, the I^1A_u—^1A_g and I^3A_u—^1A_g transitions have been located, and evidence for the I^1B_g—^1A_g and I^3B_g—^1A_g transitions has also been discussed.[8]

By analogy with glyoxal and biacetyl, the sharp band at 27189 cm.$^{-1}$ which is the origin of the vibrational analysis is assigned to the 0–0 band of the $I^1A_u \leftarrow {}^1A_g$ transition of the *trans* (C_{2h}) form of $(ClCO)_2$. The bands show evidence of predissociation in the I^1A_u state, since they become increasingly broad at higher frequencies. The continuous absorption background is assigned to an electronic transition of the *cis* (C_{2v}) form of $(ClCO)_2$. The allowed $I^1B_1 \leftarrow {}^1A_1$ transition is perhaps the most probable assignment for the continuum. The excited electronic state of the *cis*-form appears to be repulsive, since only continuous absorption can be attributed to the *cis*-form.

Illumination of the vapor with λ 3660 Å. and/or λ 3130 Å. from a high pressure mercury arc did not give any detectable fluorescence. Since no emission was obtained from the upper state, it is difficult to determine with certainty whether the origin of the vibrational analysis is really the 0–0 band of an allowed transition. It is also possible that the sharp bands may be due to more than one electronic transition. In view of the limited amount of information which can be obtained from the absorption spectrum alone, the detailed assignments must be considered as somewhat uncertain.

d. **Assignment of the Vibrational States.**—Vibrational selection rules predict that only totally symmetric (A_g) modes will be prominent in an allowed electronic transition.[11] The main progression of 1420 to 1460 cm.$^{-1}$ is therefore assigned to the (A_g) C=O stretching frequency in the I^1A_u state of the C_{2h} form. The corresponding frequency in the ground state is 1778 cm.$^{-1}$.[4] The change in frequency of this mode is comparable to the corresponding change in $(CHO)_2$ and $(CH_3CO)_2$.[8] Although the main progression may possibly correspond to the A_g C–C stretching frequency (1078 cm.$^{-1}$ in the ground state), the comparison with $(CHO)_2$ and $(CH_3CO)_2$ definitely favors the assignment of the main progression to the (A_g) C=O stretching frequency.

The excited state vibrational frequency of 397

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(9) It was found that an irreversible thermal reaction does occur if the oxalyl chloride is heated at 450° for 15 minutes. Under such conditions, the sharp structure does not reappear when the sample is cooled. However, the sharp structure does reappear if the initial heating does not exceed 275°.

(10) H. L. McMurry, *J. Chem. Phys.*, **9**, 241 (1941).

(11) H. Sponer and E. Teller, *Rev. Mod. Phys.*, **13**, 75 (1941).

cm.$^{-1}$ very probably corresponds to the ground state vibrational frequency of 494 to 509 cm.$^{-1}$ which has been deduced from the vibrational analysis, which in turn correlates with the polarized Raman band or bands appearing in the region 450–490 cm.$^{-1}$ in liquid $(ClCO)_2$. ZMCD[8] and SK[4] do not agree about the number of bands or the assignments in this region of the Raman spectrum. All workers agree that the Raman bands in this region are polarized. Nevertheless, ZMCD have assigned a B_g fundamental at 483 cm.$^{-1}$, basing their conclusions principally on the results of a normal coördinate analysis. Saksena, Kagarise and Rank,[12] have discussed this and other shortcomings of ZMCD's interpretations, and it appears that this aspect of ZMCD's assignment is untenable. This vibration has been assigned by SK to an A_g COCl deformation.

The intervals 77 and −85 cm.$^{-1}$ deduced from the vibrational analysis probably correspond to 1–1 transitions of low vibration frequencies of $(ClCO)_2$. The A_u torsional frequency, which has not been located with certainty in the infrared spectrum, and the A_g COCl rocking (276 cm.$^{-1}$) may be the vibrations which are responsible for these difference frequencies.

e. Comparison with Biacetyl and Glyoxal.—In the n—π^* transitions in glyoxal, biacetyl, and oxalyl chloride, an electron is excited from a nonbonding orbital localized on the O atom to a π^* antibonding orbital which extends over the OCCO skeleton.[8,10] Although the transition may be formally allowed by symmetry, as is definitely the case in $(CH_3CO)_2$ and $(CHO)_2$, the intensity is nevertheless low. The reasons for the low intensity of n—π^* transitions of azines have been discussed by Orgel,[13] and similar considerations apply to the OCCO chromophore.

The I^1A_u—^1A_g transition in $(ClCO)_2$ is shifted approximately 4000 cm.$^{-1}$ to higher frequencies relative to the corresponding transitions in $(CHO)_2$ and $(CH_3CO)_2$. This is to be expected in an n—π^* transition, as has been discussed by Orgel.[13]

SK[5] have noted the greater length of the C–C bond in $(ClCO)_2$ relative to $(CHO)_2$ and $(CH_3CO)_2$, and have correlated this with the smaller double bond character and greater degree of freedom of rotation around the central bond. As expected, the ground state C–C stretching frequency is considerably lower in $(ClCO)_2$ (1078 cm.$^{-1}$ [4]) than in $(CHO)_2$ (1205 cm.$^{-1}$ [7]) or in $(CH_3CO)_2$ (1280–1300 cm.$^{-1}$ [8]).

In summation, both the similarities and the differences in the spectra of these molecules appear to be explicable in terms of their molecular structure, and the spectroscopic properties of the OCCO chromophoric group support the predictions of the simple LCAO–MO theory.

Acknowledgments.—I am grateful to Professor A. B. F. Duncan for several interesting discussions. I thank Mr. C. A. Whiteman, Jr., for recording the absorption spectrum on the Cary spectrophotometer.

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(12) B. D. Saksena, R. E. Kagarise and D. H. Rank, *J. Chem. Phys.*, **21**, 1613 (1953).

(13) L. E. Orgel, *J. Chem. Soc.*, 121 (1955).

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Entropy of Krypton Adsorbed on Titanium Dioxide (Anatase)

BY E. L. PACE, W. T. BERG AND A. R. SIEBERT

RECEIVED OCTOBER 22, 1955

Calorimetric measurements of the heat capacity, adsorption isotherms and heat of adsorption between 12 and 140°K. have been used to determine the zero point entropy of krypton adsorbed on titanium dioxide of the anatase form. The zero point entropy for 0.00765, 0.01396 and 0.02421 mole of adsorbed gas corresponding to the monolayer fractions 0.13, 0.23 and 0.40 are, respectively, 1.1 ± 1.1, 1.5 ± 0.6 and 1.3 ± 0.3 cal. deg.$^{-1}$ mole^{-1}. The results indicate strongly that thermodynamic equilibrium has not been attained between the surface and the adsorbed gas. The experimental procedure which was used as well as theoretical consideration leads one to believe that most of the randomness in the system existing at approximately 50°K. was preserved at temperatures below this value.

In recent years, some investigations have been carried out in which calorimetric measurements of adsorption isotherms, heats of adsorption and heat capacity have been used to determine the entropy of a gas adsorbed physically on a solid surface. Morrison, *et al.*,[1] have carried out such a study with the argon–rutile system and Aston and co-workers[2] with the neon–rutile system. In both cases, the conclusion was reached that the zero point entropy of the adsorbed gas was zero within the experimental error, thus indicating adsorption processes in thermodynamic equilibrium.

The present investigation is concerned with krypton adsorbed on titanium dioxide of the anatase form. Considering the fact that at the same temperature the mobility of krypton on a solid surface is lower than argon and neon, the question naturally arises as to whether the adsorbed krypton would attain thermodynamic equilibrium with the surface under experimental conditions similar to those employed in the studies with argon and neon.

Experimental

The krypton was purchased from the Air Reduction Sales Company, Jersey City, New Jersey. Mass spectrographic analyses furnished with the gas indicated a purity of more than 99.9%.

The anatase used in the research was obtained from Dr. W. K. Nelson of the National Lead Company, South Amboy,

(1) J. A. Morrison, J. M. Los and L. E. Drain, *Trans. Faraday Soc.*, **47**, 1023 (1951).

(2) R. J. Tykodi, J. G. Aston and G. D. L. Schreiner, THIS JOURNAL, **77**, 2168 (1955).