and Millar[12] reports its entropy as 12.7 ± 2.0 units.

At temperatures above the melting point of the oxide, there are no data on either its heat capacity or its composition. And since the heat effect at the gamma–delta transformation is quite small, the equilibrium involving solid iron and molten oxide may be represented by the following simple equation in which "FeO(l)" represents a quantity of the liquid oxide containing 16 g. of oxygen

$$\mathrm{FeO(l)} + \mathrm{H_2} = \mathrm{Fe}(\gamma \text{ or } \delta) + \mathrm{H_2O}$$
$$\Delta F^\circ = -7240 + 4.67T \qquad (10)$$

The heat of fusion of wüstite is found from the two free energy equations to be 10,000 calories per mole. Here the "mole" contains 16 g. of oxygen but only 53 g. of iron below the melting point and an undetermined amount in the liquid. The calculated heat thus includes the effect of any change in composition of the oxide. It may be pointed out that this is less than half the magnitude of the heat effect calculated from the data of Jominy and Murphy,[17] the discrepancy arising from disagreement in equilibrium data above the melting point of the oxide.

Summary

The equilibrium of iron and its oxide with steam and hydrogen has been investigated in the range 1200–1515°.

Below the melting point of the oxide the new results and those of Emmett and Shultz are expressed by an equation which agrees essentially with the data of Jominy and Murphy.

Above the melting point the value of $K = P_{\mathrm{H_2O}}/P_{\mathrm{H_2}}$ is given by: $\log K = 1583/T - 1.021$.

The melting point of the equilibrium oxide was found to be 1369°; its heat of fusion 10,000 calories per mole.

The melting points of oxygen-free and oxygen-saturated iron were found to be, respectively, 1535° and 1524°.

CAMBRIDGE, MASSACHUSETTS
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[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 723]

An Investigation of the Complex Structure of the O–H Harmonic Bands of Substituted Alcohols, and of the Effect of Temperature on the Relative Intensities of the Multiplet Components

BY LLOYD R. ZUMWALT AND RICHARD M. BADGER

It has been observed that the fundamental and harmonic O–H vibration bands of alcohols and substituted phenols frequently consist of two or more components even in cases of substances which have only one hydroxyl group per molecule.[1,2,3] When this multiplet structure persists under conditions such as to exclude association it has often been attributed to the presence of two or more molecular species with slightly different O–H frequencies. These different species have usually been supposed to represent merely different stable molecular configurations which result from restricted rotation about one or more single bonds.

Such an explanation, however useful in some cases, must be subject to some suspicion and cannot finally be accepted without further tests since in some cases the apparent complexity of the O–H bands is probably due merely to an accidental near superposition of other harmonic or combination bands. In other instances a multiplet band may represent merely a band sequence, as has been shown to be true of the N–H bands of pyrrole.[4]

The criteria by which complex O–H bands due to the presence of several molecular species may be recognized are as follows. First, a similar pattern should be found in fundamental and harmonic regions, but the separations between the components should be roughly proportional to the number of the harmonic. Second, the relative intensities of the components should, in general, be dependent on the temperature, provided of course that equilibrium between the various molecular species is established. Third, the individual bands making up a multiplet should have different rotational structures. Pauling's explanation of the *o*-chlorophenol spectrum[5] stands up under the first two tests. The third criterion seldom can be

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(1) Wulf and Liddel, THIS JOURNAL, **57**, 1464 (1935).

(2) Badger and Bauer, *J. Chem. Phys.*, **4**, 711 (1936).

(3) Barchewitz and Freymann, *Compt. rend.*, **204**, 1728 (1937).

(4) Zumwalt and Badger, *J. Chem. Phys.*, **7**, 629 (1939).

(5) L. Pauling, THIS JOURNAL, **58**, 94 (1936).

applied for obvious reasons, but in the case of ethyl alcohol the two components of the O–H bands have obviously quite different structures.[2]

In some simple cases the number of components observed in the O–H bands agrees with the number of stable molecular configurations which are predicted by very reasonable considerations, but unfortunately many of the substances whose spectra have been studied are too complicated to permit of a detailed discussion at present. In view of the present interest in hindered rotation around single bonds, it has seemed worth while to study a number of substances so simple that the observations may be capable of a unique interpretation. To avoid complications due to the solvent and to possible association the investigations have been made on the vapor. Furthermore, in order to give additional support to the explanations invoked, a quantitative study of the temperature effect on the relative intensities of the components of the multiplets has been carried out in three cases. A qualitative study of the effect of temperature on *o*-chlorophenol[6] has already been made, but the small separation between the bands in the fundamental region appears to introduce some difficulty in drawing any quantitative conclusions. Consequently this substance has been included in our investigations with results which are very interesting.

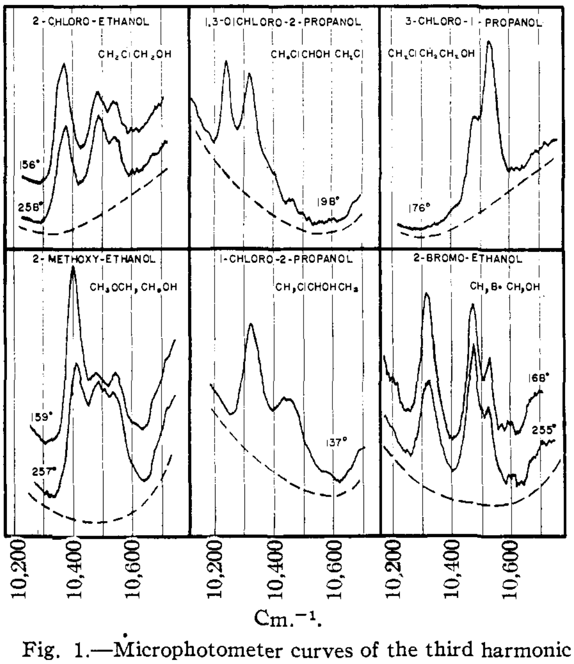

Fig. 1.—Microphotometer curves of the third harmonic O–H absorption bands of the vapors of six substituted alcohols. The temperature of the vapor is indicated in the diagrams. The dashed lines represent the trend of the background blackening.

Materials.—The substances investigated were all Eastman Kodak Co. products unless otherwise specified and the boiling points given are corrected to 760 mm. pressure. The propylene chlorohydrin, ethylene bromohydrin, trimethylene bromohydrin, and *o*-chlorophenol (b. p. 174.3° at 749 mm.) were used without further purification. The refractive indices of the first three were found to be $n^{20.6}_{D}$ 1.4370, $n^{20.5}_{D}$ 1.4928 and $n^{24.5}_{D}$ 1.4885, respectively. The propyl alcohol ("practical"), ethylene chlorohydrin, 2-methoxyethanol (Mefford Chemical Company), and *sym*-glycerol dichlorohydrin ("practical") were purified by fractional distillation and boiled at 97.2, 128.9, 124.1 and 174.4°, respectively.

Measurement of the boiling points of *o*-chlorophenol under reduced pressure gave its entropy of vaporization at 175° as 21.9 cal./deg.

Apparatus and Experimental Procedure.—This investigation was carried out with the use of a Littrow glass spectrograph with a dispersion of about 70 Å. per mm. at λ 9000. Eastman 144-Q and 1-Z infrared plates were used. The absorption spectra were obtained at about one atmosphere with a path length of three meters.

Microphotometer curves for the bands of each alcohol were obtained as well as the curves for plates exposed when the absorption cell was filled with water vapor and when the absorption cell was empty. The latter were taken to get the positions and shapes of the water absorption bands (which might be superimposed on alcohol O–H bands) and to get the curve corresponding to background blackening. The sensitivity of the 144-Q plates changes very markedly with wave length in this region.

Results of Studies on the Substituted Alcohols.—The absorption maxima of the substituted alcohols studied are listed in Table I. Figure 1 gives the microphotometer curves of the O–H third harmonic bands of these alcohols. The microphotometer curves are uncorrected for change in plate sensitivity with wave length. The dashed line below the curves indicates the trend of the background blackening. The different observed trends correspond to different batches of plates used. The only appreciable water vapor absorption occurs always at frequencies a little higher than those of the alcohol O–H

TABLE I

ABSORPTION MAXIMA IN THE O–H THIRD HARMONIC BANDS OF THE VAPORS OF SEVEN SUBSTITUTED ALCOHOLS

Substance	Absorption maxima (cm.⁻¹)		
2-Chloroethanol	10,367	10,485	10,546
2-Bromoethanol	10,318	10,470	10,527
2-Methoxyethanol	10,394	10,472	10,538
3-Chloro-1-propanol	10,467	10,525	
3-Bromo-1-propanol	10,470	10,529	
1-Chloro-2-propanol	10,326	10,460	
1,3-Dichloro-2-propanol	10,243	10,325	

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(6) M. M. Davies, *Trans. Faraday Soc.*, **34**, 1427 (1938).

vibrations. The ordinates of the microphotometer curves do not have any absolute significance as they were obtained with different microphotometer settings, plate blackenings, and concentrations of the absorbing substance.

Substituted Ethanols.—From the above data it is evident that the two O–H bands which Badger and Bauer[2] found to be characteristic of primary alcohols persist in 2-methoxyethanol, ethylene chlorohydrin, and ethylene bromohydrin, though there is a slight shift to higher frequencies and considerable change in relative intensities. The weaker component has apparently become the stronger. These two bands we may attribute to molecular configurations in which the environment of the O–H group is similar to that in ethanol. In addition, however, a new strong band has appeared at a frequency around 100 cm.$^{-1}$ lower.[6a]

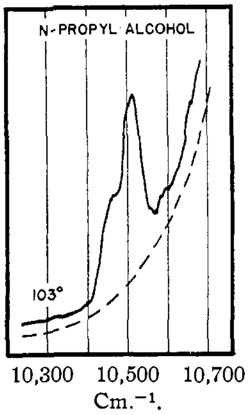

Fig. 2.—Microphotometer curve of the third harmonic O–H absorption bands of *n*-propyl alcohol.

The new band appears to be analogous to the strong long wave component which appears in the O–H bands when a halogen is substituted in the ortho position in phenol. We attribute it to chelation in a five-membered ring through the formation of a hydrogen bond between hydroxyl oxygen and other oxygen, chlorine, or bromine as the case may be. In the three compounds studied the new band is found at increasingly long wave lengths in the order just given, which is reminiscent of the observations of Wulf, Liddel and Hendricks[7] on ortho substituted phenols. As has previously been shown[8] the progressive shift to lower frequencies is an indication of increasing strength of hydrogen bond. Of the series studied the oxygen to oxygen bond appears to be the weakest and the oxygen to bromine the strongest. Possibly this is to be attributed to the differences in size of the electronegative atoms, permitting closest approach to the hydroxyl oxygen in the case of bromine.

As mentioned above, it is evident that in the substituted ethanols two types of configuration have reasonable stability in which the environment of the hydroxyl hydrogen is similar to that found in the unsubstituted primary alcohols. These configurations, however, must be less stable than the chelated structure. This is indicated by the great intensity and low frequency of the new band. Moreover, this is supported by the effect of temperature, which may be seen in Fig. 1. With increasing temperature the intensities of the short wave bands increase greatly at the expense of the low frequency component showing that they correspond to higher energy states. The temperature effect will be discussed more quantitatively below.

Substituted Normal Propyl Alcohols.—Both trimethylene chlorohydrin and trimethylene bromohydrin have O–H bands which appear to be identical with those of ordinary primary alcohols. It seems surprising that there is no indication of a hydrogen bond between halogen and oxygen with the formation of a six-membered ring, but such is the case. We may conclude that in configurations in which the oxygen halogen distance is favorable for the formation of a hydrogen bond the strain arising from the hindered rotation about the C–C single bonds is too great to permit the bond to be formed.

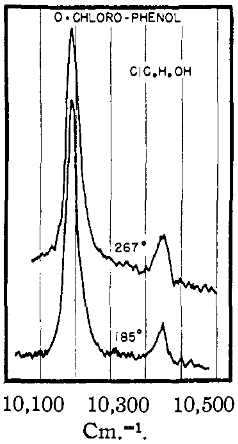

Fig. 3.—Microphotometer curve of the third harmonic O–H absorption bands of *o*-chlorophenol at two temperatures.

Substituted Secondary Alcohols.—Propylene chlorohydrin has the rather broad band characteristic of secondary alcohols and in addition a narrower, more intense component at lower frequencies. The latter may again be attributed to a chelated form with a five-membered ring involving a hydrogen bond between oxygen and chlorine.

On the substitution of the second chlorine in *sym*-glycerol dichlorohydrin the ordinary second-

[6a] Wall and Claussen [THIS JOURNAL, **61**, 2679 (1939)] failed to find any very definite evidence of chelation in ethoxyethanol and believed that they had shown its absence. They could, however, hardly expect to resolve the bands due to chelated and unchelated molecules which in this case should be separated in the fundamental region, by less than 30 cm.$^{-1}$. The chelation should undoubtedly be less in carbon tetrachloride solution than in the vapor but the curves of Wall and Claussen taken at high dilution indicate that it is not entirely absent since the band they observed is shifted to slightly longer wave lengths than normal and seems rather broad.

(7) Wulf, Liddel and Hendricks, THIS JOURNAL, **58**, 2287 (1936).

(8) Badger and Bauer, *J. Chem. Phys.*, **5**, 839 (1937).

ary alcohol band has been reduced to a mere trace while a third, new component appears at quite low frequency. We suggest that the 10,325 cm.$^{-1}$ band, as in propylene chlorohydrin, corresponds to a situation in which a hydrogen bond links the hydroxyl oxygen to one chlorine atom, while the 10,243 cm.$^{-1}$ band results from a situation in which the hydroxyl hydrogen interacts with both chlorine atoms. In the latter case we have a double ring chelation.[9]

Investigation of the Temperature Effect.—A quantitative photometric investigation was conducted of the effect of temperature on the relative intensities of the components of the O–H bands of *o*-chlorophenol, ethylene chlorohydrin and propyl alcohol. These experiments involved the keeping of the absorption cell at constant temperature and the regulation of the pressure of the vapor within the cell. The temperature of the cell was read by means of a thermometer inserted in a well in its midsection and could be kept constant by means of automatic voltage control on the heating circuit. It is believed that the actual temperature of the vapor was within three or four degrees of the corrected thermometer readings. The pressure of the vapor was controlled by regulating the temperature of a side tube which contained an excess of liquid and was at all times cooler than the absorption cell. In the experiments on *o*-chlorophenol the side tube dipped in a well agitated oil-bath, the temperature of which was constant to within two-tenths of a degree. In the other cases an auxiliary furnace was used.

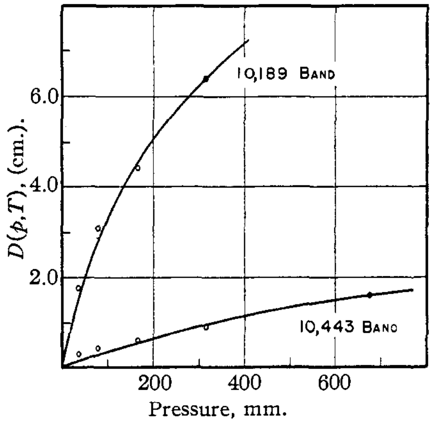

Fig. 4.—A plot against pressure of the microphotometer deflections $D_t(p,T)$ and $D_c(p,T)$ for the *o*-chlorophenol bands at 10,443 cm.$^{-1}$ and 10,189 cm.$^{-1}$, respectively. The data were obtained from a group of exposures taken on one plate with the vapor at approximately 180°, and at a series of pressures.

In estimating the pressure of the vapor, data in the "International Critical Tables" were used except in the case of *o*-chlorophenol. As mentioned above, the boiling point of this substance was observed at several pressures.

The Photometric Procedure.—Precise photometry in the infrared with ammoniated plates is rather difficult, but a simplified procedure was devised which worked quite well. It involves certain assumptions which are discussed below, but these seem to be well justified and unlikely to introduce any large error. Difficulties due to the non-uniformity of the plates were largely avoided by taking all exposures of a complete series on one and the same plate, and indeed on a strip down the center of the plate where sensitization was most uniform. All exposures of a series were taken with constant illumination and equal exposure times. The warping of the absorption cell as the temperature was changed necessitated a slight compensating adjustment of one mirror in the optical train, but a fairly satisfactory constancy of background blackening through a series was attained.

Each series of exposures included two groups taken at two temperatures of the absorption cell, T_1 and T_2, respectively, and each group usually included spectra taken at several different pressures. The entire set of spectrograms was run through the microphotometer with the sensitivity of that instrument kept constant.

The interpretation of a series of records will now be described with special reference to *o*-chlorophenol. The difference between the microphotometer deflections at the band maximum and the deflection corresponding to background blackening was taken as a measure of the intensity of a band. This quantity, which is a function of pressure and temperature, we shall designate by $D_c(p,T)$ or $D_t(p,T)$ when referring, respectively, to the 10,189 cm.$^{-1}$ band (arising from molecules in the *cis* form) or the 10,433 cm.$^{-1}$ band of *o*-chlorophenol (arising from *trans* molecules). A plot of these quantities against pressure for a group of exposures taken at approximately 180° may be seen in Fig. 4.

Now the investigations of Wulf and Liddel[1] in the second harmonic region have shown that the total integral molal absorption coefficient for the

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[9] The crystal structure of glycine indicates the occurrence of a somewhat similar situation in which one of the hydrogen atoms of the NH_3^+ group is attracted about equally strongly by two oxygen atoms; see Albrecht and Corey, This Journal, 61, 1087 (1939).

two O–H bands of *o*-chlorophenol is practically the same as for the one band of phenol and also for the one band of 2,4,6-trichlorophenol. From this it is most reasonable to conclude that the transition probabilities are practically the same for the *cis* and *trans* forms of *o*-chlorophenol, and that the concentrations of the two forms are in the ratio of the intensities of their corresponding bands.

Owing to experimental difficulties it was not possible to determine integral absorption coefficients or to compare directly the intensity of the two bands. However, if at any given temperature, T_1, the intensity of the "*cis*" band at pressure p_1 is the same as that of the "*trans*" band at p_2, it is evident that the ratio of *cis* and *trans* forms of the molecule at T_1 is given by $(n_c/n_t) = (p_2/p_1)$.

High dispersion studies have shown that the two bands have practically the same shape and breadth.[2] Furthermore, the IZ plates used have a sensitivity which is very nearly constant with wave length over a considerable range. Consequently when $D_c(p_1,T)$ and $D_t(p_2,T)$ are equal the intensity of the "*cis*" band at p_1 is equal to that of the "*trans*" band at p_2 to a good approximation.

It follows that the two curves of Fig. 4 should be practically superposable if the abscissas of the curve corresponding to the 10,443 cm.$^{-1}$ band are reduced by an appropriate factor s. Consequently we may write $(n_c/n_t) = (1/s)$, and the free energy increase for the transformation

$$o\text{-chlorophenol } (cis) \longrightarrow o\text{-chlorophenol } (trans) \quad (1)$$

is given by the equation

$$\Delta F = RT \ln (n_c/n_t) = RT \ln (1/s) \quad (2)$$

The energy increase for the same transformation is given by

$$\Delta E = \frac{T_2T_1}{T_2 - T_1} R \ln \frac{(n_c/n_t)_{T_1}}{(n_c/n_t)_{T_2}} = \frac{T_2T_1}{T_2 - T_1} R \ln \frac{(1/s)_{T_1}}{(1/s)_{T_2}} \quad (3)$$

The evaluation of this expression involves obtaining data at a second temperature T_2. Fewer measurements were made at the higher temperatures owing to greater difficulty in keeping steady conditions, and consequently it was assumed that the shapes of the $D(p,T)$ curves were the same at T_2 as at T_1. This assumption is good unless the *shape* of the band envelopes differs considerably at the two temperatures. This can scarcely be the case. The bands will broaden slightly with temperature but the shape of the envelopes should not change materially.

In the evaluation of the energy difference between *cis* and *trans* forms of the molecule it is not necessary to assume equal transition probabilities for the two molecular species and equal widths and shapes of the two bands. This results from the fact that equation 3 involves the ratio of two concentration ratios.

Possibly the largest error in the determinations arises from the difficulty in precisely estimating the $D(p,T)$ quantities, due to the grain of the plate. This is particularly true in the case of the weaker band where the error of measurement may be as large as 20%.

Results of the Measurements of Temperature Effect.—Three preliminary experiments I, II and III were made on *o*-chlorophenol, and two more extensive studies, IV and V. These are summarized in Table II.

TABLE II

PHOTOMETRIC STUDY OF *o*-CHLOROPHENOL

$D_t(p,T)$ (cm.)	$D_c(p,T)$ (cm.)	T(°K.) of vapor	p(mm. Hg.) of vapor	$\Delta F°$ (kg.-cal./mole)	$\Delta E°$ (kg.-cal./mole)
		Expt. I			
0.43	3.90	453	255	2.2	
.57	5.70	453	410		
.70	3.56	542			4.3
.96	5.05	543			
		Expt. II			
0.73	4.22	459	133		
.83	5.24	459	192	2.6	
.94	6.16	459	281		
1.37	6.50	539			3.5
		Expt. III			
0.56	4.30	457	146		
.78	5.39	458	232	2.6	
.89	6.49	458	334		
.90	5.20	540			2.8
1.09	5.87	540			3.7
		Expt. IV			
0.40	1.99	460	32.6		
.43	3.41	460	79.3		
.61	4.37	461	160	3.0	
.98	6.42	461	301		
1.53	..	463	638		
0.92	4.53	534			4.3
.79	4.29	537			3.6
.87	4.50	537			3.8
		Expt. V			
0.30	1.76	450	36.7		
.50	3.10	450	78.5		
.62	4.42	451	166	2.7	
.91	6.39	450	314		
1.60	..	451	676		
0.70	3.25	537			4.5
.60	2.87	537			4.6
.58	3.14	537			3.6
			Weighted av.	2.8	3.9

An average of the several determinations shows that in the temperature range covered the energy increase for the *cis–trans* transformation is 3.9 ± 0.7 kgcal. per mole. For the same reaction the free energy increase is 2.8 ± 0.5 kgcal. per mole and the entropy increase 2.4 E. U. at 180°.

In the study of *n*-propyl alcohol it was found that the change in intensity ratio of the two O–H bands is practically within experimental error. From this we estimate that the difference in energy of the two hypothetical configurations is not greater than about 0.8 kgcal. per mole.

In ethylene chlorohydrin, also, the relative intensities of the two bands characteristic of primary alcohols did not change appreciably. Consequently the data in Table III were used to determine the difference between the average energy of the forms corresponding to these bands and the energy of the chelated structure. The former was found to exceed the latter by 2.0 ± 0.5 kgcal.

TABLE III

PHOTOMETRIC STUDY OF ETHYLENE CHLOROHYDRIN

$D_a(p,T)^a$ (cm.)	$D_b(p,T)^a$ (cm.)	$D_c(p,T)^a$ (cm.)	T(°K.) of vapor	p(mm. Hg.) of vapor	$\Delta E°$ (kg.-cal./mole)
			Expt. I		
1.00	1.61	2.87	425	490	
1.22	1.89	3.29	425	646	1.9
2.05	2.96	4.90	425	1048	
1.42	2.22	2.60	531		
			Expt. II		
1.00	1.72	2.87	420	417	
1.65	2.40	3.99	421	709	2.1
2.29	3.42	5.12	421	1120	
0.87	1.32	1.70	516		
					Av. 2.0

[a] The quantities D_a, D_b and D_c refer to the ethylene chlorohydrin absorption maxima at 10,546, 10,485 and 10,367 cm.$^{-1}$, respectively.

Discussion of the Studies on Temperature Effect.—Badger and Bauer have pointed out that there appears to be a convenient relation between the frequency shift in the O–H bands which takes place on the formation of a hydrogen bond and the energy of the bond. In a letter which will be published soon it will be shown that the data here reported confirm the existence of this relation, which will now be applied in a discussion of *o*-chlorophenol.

Our value of 2.8 kgcal. for the free energy difference between *cis* and *trans* forms of *o*-chlorophenol in the vapor state at 180° may at first seem in disagreement with the estimate of 1.4 kgcal. given by Pauling for the substance in carbon tetrachloride solution at room temperature. There is, however, no reason to suppose that this is the case. The percentage frequency difference between the two bands of the substance in solution indicates a difference in energy of two forms of only about 2.9 kgcal. as against our value of 3.9 kgcal. for the vapor. This apparent discrepancy is to be accounted for by the stabilizing effect of the solvent on the *trans* form. When the vapor of a normal alcohol is dissolved in carbon tetrachloride the shift in O–H frequency indicates an energy of interaction between solvent and the hydroxyl group of between one and two kgcal. Consequently it is not surprising that *trans* *o*-chlorophenol is stabilized to about this extent in carbon tetrachloride solution.

The considerable difference in entropy of the *cis* and *trans* forms is rather surprising. It appears difficult to account for it entirely in terms of the torsional oscillations of the hydroxyl hydrogen about the two potential minima. In the explanation of the double O–H bands of *o*-chlorophenol it has been assumed that there are two distinct molecular species present or, in other words, that the energy levels of the *o*-chlorophenol molecule may be divided into two classes which may be ascribed to molecules in which the hydroxyl hydrogen is performing torsional vibrations about the *cis* or *trans* minima, respectively. It does not seem possible to construct a potential function for the rotation of the hydrogen about the C–O bond which will yield a sufficient number of levels of the second class to account for the entropy difference. It is possible that the high frequency band is partly due to molecules in which the hydrogen is performing complete rotations. In the lower lying levels for which this is the case the atom will spend most of its time on the side of the molecule opposite the chlorine atom, owing to the broad shallow character of the upper minimum. For this reason the O–H frequency in this species of molecule might not differ greatly from that in a vibrating *trans* molecule.

However, a portion, and perhaps the main part, of the entropy difference may be due to another factor. In the *cis* molecular species at least two bending vibrations must have considerably higher frequencies than in the *trans* form, owing to the contribution of the hydrogen bond to the rigidity of the chelated structure.

Summary

1. An investigation has been made of the complex structure of the third harmonic O–H bands of ethylene chloro and bromohydrin, methyl cellosolve, trimethylene chloro and bromohydrin, propylene chlorohydrin, and *sym*-glycerol dichlorohydrin. These substances were all studied in the vapor state. In all cases except trimethylene chloro and bromohydrin the substitution of a halogen or a methoxy group in the alcohol has given rise to one or more new O–H bands.

2. Photometric studies have been made of the effect of temperature on the relative intensities of the components of the O–H bands in *o*-chlorophenol, propyl alcohol and ethylene chlorohydrin. It is found that in the vapor state at 180° the energy and free energy of the *trans* form of *o*-chlorophenol exceed those of the *cis* form by 3.9 ± 0.7 and 2.8 ± 0.5 kgcal., respectively.

PASADENA, CALIF. RECEIVED AUGUST 28, 1939

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Allylic Rearrangements. X. The Reproducibility of the Standard Methods for the Preparation of Butenyl Bromide Mixtures[1]

BY WILLIAM G. YOUNG AND KENZIE NOZAKI

As a result of a recent study[2] of the composition of butenyl bromide mixtures obtained from crotyl alcohol and methylvinylcarbinol by the action of various solutions of hydrogen bromide *under controlled conditions*, a mechanism was proposed for the reaction[3] in which two simultaneous processes were considered. Process 1 assumed an opportunity for resonance of the reacting oxonium ion of the alcohol and hence for the formation of the same mixture of bromides from either the primary or secondary alcohols. Process 2, a normal substitution without resonance, gives only primary bromide from the primary alcohol and secondary bromide from the secondary alcohol. Since the values calculated for M (the fraction of alcohol reacting by Process 2), N_r (the refractive index of the bromide mixture formed by Process 1) and P_r (the percentage of primary bromide in the bromide mixture formed by Process 1 due to resonance) are dependent on the accuracy with which the composition of the butenyl bromide mixtures (prepared by the various standard methods) can be determined, it is highly desirable to test the reproducibility of the standard methods; especially since we have continually pointed out the difficulties encountered by other workers due to the extreme mobility of the bromides.

The results of the present investigation are summarized in Table I along with the results previously reported.[2,3] In general, the average deviation of the refractive index of the butenyl bromide mixture obtained from the same alcohol with a given standard method is ±0.0001 although with the standard method 3 (saturated hydrobromic acid at 0°) the mean deviation is ±0.00016. Two cases were observed where the previous results were in error. The action of hydrogen bromide gas at −20° on methylvinylcarbinol gave a bromide mixture with a refractive index 0.0010 unit lower than that previously reported, showing that a small amount of rearrangement had occurred in the previous case in spite of the special precautions which were taken to avoid it. The discrepancy observed between the results obtained by method 7 (the action of glacial acetic acid saturated with hydrogen bromide at 0°) on crotyl alcohol were traced to a different cause. A preliminary run proved that insufficient time had been allowed for the reaction (twenty-five min.). Hence the product contained traces of unreacted alcohol. This was indicated by a low Carius analysis (Br = 57.7% instead of 59.2%). As a result, the rearrangement of the sample at 100°, to get the corrected refractive index, caused the formation of dibutenyl ether which lowered the refractive index of the sample. Proof of this was found when a mixture of butenyl bromides was contaminated with a quantity of crotyl alcohol comparable with that suspected to be present in the bromide mixture prepared in

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[1] This work, which was accomplished with the aid of a grant from the Board of Research of the University of California, was presented before Section C of the Pacific Division of the American Association for the Advancement of Science at Stanford University, June 29, 1939.

[2] Young and Lane, THIS JOURNAL, 59, 2051 (1937).

[3] Young and Lane, *ibid.*, 60, 847 (1938).