solutions, where but little micelle was previously present. Indeed, the micelle so formed appears to have a greatly increased solubilizing power, not only over the ordinary micelle of the same soap, but even over the same micelle in higher concentrations in the presence of the potassium chloride. Furthermore, even in the concentrated solutions, the potassium chloride has increased the solubilization. This is the opposite of the expected salting out effect. Neither can it be reconciled with the hypothesis of solution in the hydrocarbon, which must be unaffected since it is in equilibrium in all cases with solid crystals of dye. We have no adequate explanation either for the improved solubilizing power in concentrated solutions or for its still greater enhancement in dilute solutions. However, a similar effect in dilute solutions was indicated in Hartley's data for cetylpyridinium chloride with sufficient addition of sodium chloride (see reference 2, page 129). Likewise, Merrill found similar effects with pure *n*-(lauryl colamino formyl-methyl)-pyridinium chloride, commercially known as Catol 607, to which potassium chloride was added.

On the other hand, Dr. R. B. Dean in unpublished demonstrations in this Laboratory has shown that potassium chloride reduces the solubilizing power of 0.2 *m* potassium laurate for capryl alcohol. Addition of this chloride to a clear saturated solution of capryl alcohol in 0.2 *m* laurate produces a very evident turbidity, which is cleared by heating or by further addition of potassium laurate solution free from capryl alcohol.

Summary

1. The solubilization of water insoluble dye by four potassium soaps has been measured for equilibrium conditions over a range of concentrations.

2. The solubilization increases so rapidly with the higher soaps as to cast doubt upon the suggestion that it is solution in the hydrocarbon fraction of the molecule, but rather to favor its incorporation between the layers of lamellar micelles.

3. Potassium chloride not only greatly increases the solubilizing power of fully formed micelles, but it produces in dilute solution micelles of still higher solubilizing power.

STANFORD UNIV., CALIF. RECEIVED SEPTEMBER 2, 1943

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE STATE COLLEGE OF WASHINGTON]

The Ionization of Strong Electrolytes. II. Ionization, Raman Spectrum and Vibrations of Perchloric Acid

BY O. REDLICH, E. K. HOLT AND J. BIGELEISEN[1]

As discussed in the first paper of this series,[2] the Raman spectrum furnishes a fairly general and unambiguous criterion of the existence of molecules. This criterion, in addition, is cogent if one retains the historical concept of the molecule which characterizes the molecule as a mechanical unit without referring to the nature of the intramolecular forces. The principle of determining the degree of ionization by means of Raman spectra, its history, and some experimental details have also been discussed previously. In the present paper, a refinement of the experimental method and measurements on perchloric acid are reported.

In a check of the Raman frequencies of anhydrous perchloric acid, a previously missing line was discovered by resolution of a doublet. Since this line completes the spectrum of the simplified model, our results for the frequencies of perchloric acid and the perchlorate ion, and an assignment of the frequencies to the vibration forms are included.

The Experimental Method

The spectrograph and the general equipment have been described previously.[2,3] Cells of the smaller type (18 ml.) were used. The front face of the cells was ground and polished. The perchlorate line 931 cm.$^{-1}$, excited by the blue mercury line was used. Because of the instability of the acid, the violet and ultraviolet light was filtered out by a sodium nitrite solution. Exposure times ranged from three minutes with Eastman Kodak Co. plates 103a-O and a slit width of 0.10 mm. to twenty-four minutes with plates II-O and 0.25 mm.

Like the nitrate line, the perchlorate line is fairly sharp and narrow in solutions of sodium perchlorate and in the practically completely ionized acid solutions of moderate concentrations, but considerably broader in concentrated solutions of the acid. Several attempts were made to diminish the error involved in the photographic comparison of the intensity of lines which appreciably differ in width.

For convenience, the usual way of comparing the areas under the microphotometric curves will be called the first method. This method can be considered to be based on two assumptions: (a) that under appropriate experimental conditions, the microphotometric curves of two lines are equal only if the total intensities striking the plate are equal, and (b) that a microphotometric curve is sufficiently characterized by its area.

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[1] Present address: Department of Chemistry, Columbia University, New York, N. Y.

[2] O. Redlich and J. Bigeleisen, THIS JOURNAL, **65**, 1883 (1943).

[3] O. Redlich and L. E. Nielsen, *ibid.*, **65**, 654 (1943).

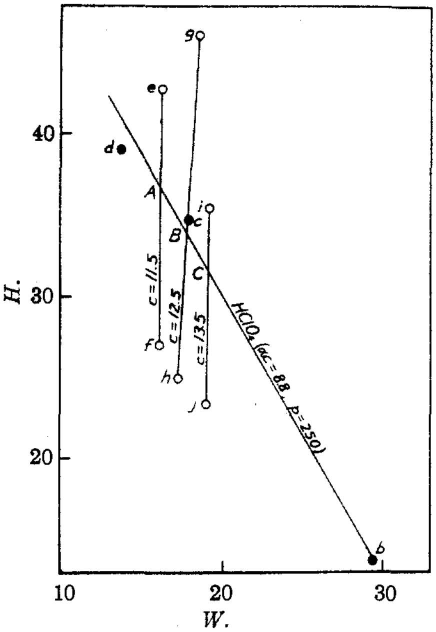

Fig. 1.—Second method: diagram of heights H and widths W of the microphotometric curves.

The first assumption can hardly be dispensed with in any photographic method. The second can be replaced by a less far reaching one: that a microphotometric curve is sufficiently characterized by its height H and width W, measured as usual at the level $H/2$. This assumption is supported by our experience that the area under the curves is practically proportional to the product HW.

The resulting "second method" consists in a comparison of microphotometric curves by interpolation with respect to the two independent variables H and W.

The practical procedure is conveniently described in an example (Fig. 1). The intensity of the light striking the plate is proportional to $I = \alpha cfw$, where αc is the concentration of the perchlorate ion, f the value of the stepfilter before the spectrograph slit, and w the width of this slit. Diffraction at the slit[4] is entirely negligible under the prevailing conditions. The calibration was carried out by means of a perchloric acid solution containing 8.9 moles per liter, corresponding to $\alpha c = 8.8$ according to the smooth curve of Fig. 2 (usually sodium perchlorate solutions were used for calibration). The points b, c and d were taken with different slit widths ($w = 0.250$, 0.323 and 0.595 mm.) but the product $p = fw$ was the same. The points e to j were all taken with $w = 0.250$, but p was 250 for e, g and i, and 194 for f, h, and j.

According to the basic assumptions of the second method, the intensity $I = \alpha cp$ at the crossing point A can be expressed in terms of both the calibrating solution ($\alpha c = 8.8$; $p = 250$) and the "unknown" solution (αc to be determined; $p = p_A$). Thus we have for the "unknown" solution $\alpha c = 8.8 \cdot 250/p_A$ where p_A is to be found by interpolation from the p-values of the points e and f.

The interpolation is to be carried out either linearly with respect to the distances in the diagram or better according to $\log(HW) = k_1 + k_2 \log p$. The values of H and W are read from the diagram and the constants k_1 and k_2 are eliminated by means of the known values of p for the points e and f.

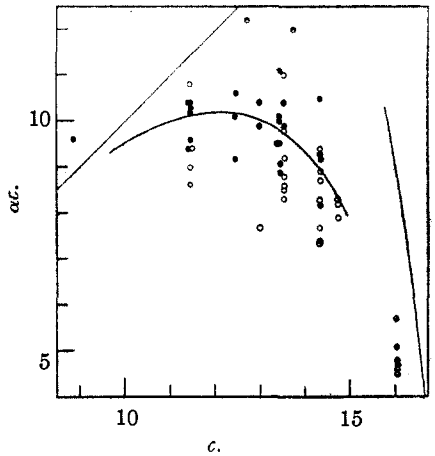

Fig. 2.—Concentration αc of the perchlorate ion in solutions of perchloric acid of the concentration c: ◒, first method, 30°; O, 53°; ◓, second method, 30°; ●, 53°.

As to be seen from Fig. 2, the results of the second method scatter somewhat less than those of the first. Some additional gain in accuracy would be attained if the lines in a diagram like Fig. 1 were defined by more than two or three points. Practically, however, the number of exposures to be taken in one series and on one plate is limited, even if exposures can be taken as short as with our equipment.

Considerable progress might be achieved by a photoelectric method with the aid of the new photomultiplier tube.[5] The intrinsic difficulties of the photographic method arise from the logarithmic response of the plate. The intensity distribution within the line is necessarily distorted by the logarithmic response of the plate, and again by the influence of the finite width of the microphotometer slit. In addition, the linear response of the microphotometer with respect to the opacity restricts the usable range of the plate to a small interval in which, moreover, the plate is not very efficient. The photoelectric tube with its immediate linear response and large range is free from these disadvantages.

Substances

After a number of unsatisfactory attempts, the following

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(4) J. Milazzo and G. B. Tommasi, *Spectrochim. Acta*, **1**, 229 (1939).

(5) R. B. Janes and A. M. Glover, *R. C. A. Review*, **6**, 43 (1941; D. H. Rank, *et al.*, *J. Opt. Soc. Am.*, **32**, 390 (1942), **33**, 31 (1943)).

TABLE I

WAVE NUMBERS AND VIBRATIONS OF $(HO)ClO_3$ AND ClO_4^-

Interpretation[a]	O(s)	O(b)	OH(s)	O(s)	O(b)	OH(b)
Symmetry type	A_1	E	A_1	E	A_1	E
$(HO)ClO_3$	(12) 1032	(5) 585	(7) 738	(3b) 1312—1182	(7) 572	(3) 425
ClO_4^- in $NaClO_4$ soln.	(20) 940	(7) 631	(6b) 1167—1053		(7) 464	
ClO_4^- in $HClO_4$ soln.	(20) 931	(8) 631	(3b) 1174—974		(8) 462	
Symmetry type	A	E	F		F	

[a] (s) and (b) denote stretching and bending vibrations, respectively.

reliable distillation conditions were established for the preparation of the anhydrous acid.[6] A mixture of 640 ml. chilled sulfuric acid and 160 ml. of chilled perchloric acid (70%) is sealed in a distilling flask and distilled at about 58° in the vacuum of an oil pump. In a period of sixteen hours, approximately 30 ml. of colorless anhydrous acid is collected in a receiver cooled by means of dry-ice. Solutions in the range between 70 and 100% can be prepared only by mixing since the boiling points are so high that the acid decomposes.

Acid of 70% was purified by distillation. Distillates were analyzed by weight titration.

Sodium perchlorate was recrystallized after the solution had been boiled with charcoal. The solutions were analyzed by evaporating in a platinum dish and drying at 150°.

The concentrations were calculated by means of the densities given in the "International Critical Tables," the values of Kohner[7] and two values which we determined with a pycnometer. The density of a solution containing 5.35 moles of sodium perchlorate per kilogram of solution was found to be 1.646 g. per ml. at 25.0°, and 1.618 at 53°.

The concentration range which had to be covered, includes the interval in which solid monohydrate appears at room temperature. Most measurements therefore were carried out at 53 ± 2°. The temperature was maintained by means of an electric hairdryer, the heater being controlled by a resistor.

Results

The results are given in Fig. 2. The straight line in the left part of the diagram indicates the limit of complete ionization. Even the commercial acid (60% or 9 moles per liter) is almost completely ionized.

The slightly curved line in the right part of the diagram indicates the ionization which would be obtained if each water molecule produced a perchlorate ion according to the equation $HClO_4 + H_2O = H_3O^+ + ClO_4^-$. The data of Fig. 2 indicate that a "complete ionization" of this kind might occur in the limit of high acid concentrations. In the case of nitric acid, this possibility was definitely excluded by the experimental data.

Considering the extreme value of the heat of dilution, one has to expect a considerable variation of the ionization with the temperature. Two exposures of moderately concentrated solutions at 30° confirmed this expectation. Similar results on nitric and iodic acids are mentioned in a recent note of Rao.[8]

The concentration range is limited by the decomposition of the acid under mercury light. For the concentration of 16.1 moles per liter, data could be obtained only at the lower temperature.

The calculation of the ionization constant according to the method used in the case of nitric acid has to be postponed, because the activity coefficients are known only in the range of practically complete ionization.

Frequencies and Vibrations

Owing to the rapid decomposition under mercury light, even if filtered, a good spectrum of anhydrous perchloric acid is difficult to secure. After several unsuccessful attempts, we obtained a strong and remarkably clear spectrum in forty minutes on an Eastman plate 103a-O with a slit width of 0.06 mm. One spectrum each of an acid solution (11.6 moles per liter) and of sodium perchlorate (9.06 moles per liter) were measured.

The results, indicated in Table I, agree fairly well with those of previous authors. There is only one significant difference: we were able to resolve a line in the spectrum of the anhydrous acid[9] into a doublet, namely, the sharp line 572 and the weaker and broader line[10] 585 cm.$^{-1}$.

This result affords a basis for revising and completing Fonteyne's interpretation of the perchloric acid spectrum. As pointed out by Fonteyne, the perchlorate ion has the tetrahedral symmetry T_d, and the acid has the trigonal symmetry C_{3v} provided the hydroxyl group is considered as a mechanical unit. This simplification implies that the three hydrogen frequencies are not taken into account.

The symmetry types according to Placzek and the interpretation of the vibrations are given in Table I. A_1 and A denote the totally symmetric types, E double, and F triple frequencies. In the transition from the acid to the ion, one hydroxyl stretching and two oxygen stretching vibrations become identical and coalesce into a triple vibration. The same holds true for bending vibrations. Thus the relations between the vibrations of the acid and the ion are unambiguously determined.

According to Fonteyne, the lines 1032 and 738 of the acid are polarized; they belong, therefore, to type A_1. The third line of this type undoubtedly is the stronger and sharper line of the doublet, namely, 572.

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(6) We are indebted to Mr. L. E. Nielsen for extensive preparatory work.

(7) H. Kohner, *Z. physik. Chem.*, **B1**, 427 (1928).

(8) C. S. Rao, *Current Sci.*, **11**, 429 (1942).

(9) (a) R. Fonteyne, *Nature*, **138**, 886 (1936); (b) *Natuurwet. Tijdschr.*, **20**, 112 (1938); (c) A. Simon and H. Reuther, *Naturwissenschaften*, **25**, 477 (1937); (d) A. Simon, H. Reuther and G. Kratzsch, *Z. anorg. allgem. Chem.*, **239**, 329 (1938).

(10) Actually the two lines are partially superimposed. Fonteyne (ref. 10b) in his Fig. 1 also indicates an asymmetric structure similar to our observation.

The assignment of line 931 of the ion is based on its intensity and polarization. This frequency results from a stretching of four oxygen bonds which can be interpreted as the result of resonance between one single and three double bonds. The corresponding symmetric oxygen frequency of the acid must be higher, the hydroxyl frequency lower; in addition, the ratio of these two frequencies resulting from double and single bonds, respectively, should be approximately $\sqrt{2}:1$. The frequencies 1032 and 738 satisfy these conditions. The same argument has been used before by Chédin[11] in the case of nitric acid.

The remaining frequency 572 of type A_1 results from a bending vibration of the oxygen atoms.

Oxygen frequencies in the range around 1200 necessarily correspond to stretching vibrations. It happens frequently that antisymmetric or degenerate stretching frequencies are higher than the symmetric ones.

Thus all stretching vibrations have been assigned and none is left for another frequency of the acid near 1200, as assumed by Fonteyne on account of a doublet found in this region in the spectrum of chlorine heptoxide.[12] This doublet, one vibration symmetric, the other antisymmetric with respect to the twofold axis of the simplified chlorine heptoxide molecule, is to be expected in the spectrum of the oxide, but not in that of the acid.

The assignment of the degenerate bending vibrations 585 and 425 is fairly safe. The hydroxyl group produces the weaker restoring force and therefore is to be correlated to the lower frequency. The two bending vibrations 572 (A_1) and 425 (E) of the acid condense to the frequency 462 (F) of the ion, while 585 (E) corresponds to 631 (E).

A very weak and uncertain line 277 in the spectrum of the anhydrous acid, 297 in the acid solution, could not be satisfactorily interpreted.[13]

The assignment presented here is consistent with Fonteyne's results on deuterium perchlorate.[14]

Summary

1. A refined photographic method of comparing the intensities of spectral lines of unequal width has been developed.

2. The degrees of ionization of perchloric acid have been determined. As to be expected, perchloric acid is ionized to a much greater extent than nitric acid. The ionization constant could not be calculated as the activity coefficients are not known in the range of high concentrations.

3. The Raman spectra of anhydrous perchloric acid and concentrated solutions of the acid and of sodium perchlorate have been measured. Fonteyne's interpretation of the vibration spectrum of the acid has been revised and completed.

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[11] J. Chédin, *J. phys. radium*, **10**, 445 (1939).

[12] R. Fonteyne, *Natuurwet. Tijdschr.*, **20**, 275 (1938).

[13] Simon, *et al.* (ref. 9d), found 284 in the anhydrous acid. The line might represent the restricted internal rotation.

[14] R. Fonteyne, *Natuurwet. Tijdschr.*, **21**, 6 (1939).

PULLMAN, WASHINGTON RECEIVED AUGUST 4, 1943

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 936]

The Heat Capacity, Heats of Transition, Fusion and Vaporization, Vapor Pressure and Entropy of 1,1,1-Trifluoroethane

BY HORACE RUSSELL, JR., D. R. V. GOLDING AND DON M. YOST

Part of the low temperature calorimetric research program of this Laboratory has been the careful determination of the entropy of simple compounds in which hindered rotation about single bonds would be expected and for which straightforward and reliable statistical mechanical calculations can be made. Of the compounds available, ethane and similar molecules with two symmetrical groups on a common axis seem best suited for study both because of their convenient boiling points and because their configurations and normal frequencies can be readily determined. The existence of a barrier of about 3000 cal./mole hindering internal rotation in ethane was established by Kemp and Pitzer and Kistiakowsky, Lacher and Stitt.[1] Work by Rubin, Levedahl and Yost[2] indicates a barrier of about 2700 cal./mole for 1,1,1-trichloroethane, CH_3CCl_3. From the results reported in this paper the barrier in 1,1,1-trifluoroethane is about 3400 cal./mole. The fact that the values for these three molecules are the same within experimental error points to the interesting and significant possibility that the barrier is a function of the type bonds formed by the carbon atom but is independent, to a first approximation at least, of the nature of the attached atoms.

Purification of CH_3CF_3 or Freon "F-143."—The material used for the measurements was part of a redistilled sample furnished through the courtesy of Dr. A. F. Benning of the Jackson Laboratory of the du Pont Co. The material was carefully dried with phosphorus pentoxide, pumped to remove a small amount of dissolved air, and then fractionally distilled at a reflux ratio of about 40:1 through a 150-cm. vacuum jacketed column packed with glass helices.

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[1] J. D. Kemp and K. S. Pitzer, THIS JOURNAL, **59**, 276 (1937); G. B. Kistiakowsky, J. R. Lacher and F. Stitt, *J. Chem. Phys.*, **6**, 407 (1938).

[2] T. R. Rubin, B. H. Levedahl and D. M. Yost, to be published.