data on similar salts. The values which Dr. Rossini obtains are +9540 and +6340 calories for potassium bromate and iodate, respectively. He estimates the uncertainties in the values for the heats of solutions at 298.1°K. to be ±140 and ±100 calories per mole, respectively. We may now calculate the entropies of solution from the relationship

$$\Delta S^\circ = (\Delta H^\circ - \Delta F^\circ)/T$$

We find that the entropy changes, in going from the salts to their respective hypothetical one molal solutions, are, respectively, 26.3 and 15.3 entropy units. These values, when added to the entropies of the respective salts, give the sum of the entropies of potassium and bromate ions, and potassium and iodate ions. Using the calculated value, 24.6 entropy units for the entropy of potassium ion,[9] we obtain the values 37.4 and 26.9 E. U. for the entropies of bromate and iodate ions, respectively. The values previously reported by Greensfelder and Latimer[10] from data on barium bromate and silver iodate have been recalculated, using revised values for the entropy of barium and silver ions:[9] these values are 38.7 and 27.7 E. U. The largest errors in all of these calculations are the heats of solution of the salts, and the direct calorimetric determinations of these heats of potassium bromate and iodate appear to be more reliable than the heats of solution obtained from temperature coefficients of solubility which were used in the case of barium bromate and silver iodate. We therefore are inclined to give more weight to our new values, and estimate their accuracy as about 1 E. U.

Since the entropy of iodate ion must be greater than that of bromate in the gaseous state, it follows that the entropy of hydration of iodate is from 10 to 15 E. U. greater than that of bromate. This is very surprising in view of the larger size of the iodate, and seems to indicate either that the iodate is much more polar so that the more negative oxygen atoms are producing greater polarization of the water molecules,[11] or that one or more water molecules have been definitely bonded to the ion to form $H_2IO_4^-$ or $H_4IO_5^-$ in the water solution.

The experimental work reported here was performed in the Chemical Laboratory of the University of California. The calculations involved were in great part completed at The Johns Hopkins University.

Summary

The specific heats of potassium bromate and of potassium iodate have been determined from the temperatures of liquid hydrogen to room temperature. The entropies of the two salts have been calculated at 298.1°K. These values have been used to calculate the entropies of bromate and iodate ions.

[9] Latimer, Schutz and Hicks, *J. Chem. Phys.*, **2**, 82 (1934).

[10] Greensfelder and Latimer, THIS JOURNAL, **50**, 3286 (1928); **53**, 3813 (1931).

[11] See Latimer and Kasper, *ibid.*, **51**, 2293 (1929).

BALTIMORE, MARYLAND
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RECEIVED JANUARY 4, 1934

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

The Dielectric Properties of Acetylenic Compounds. I. The Symmetrical Dialkyl Acetylenes

BY HERMAN H. WENZKE AND R. P. ALLARD

The zero moment found for acetylene is considered strong evidence against the existence of an appreciable portion of the acetylidene ($H_2C{=}C$) form of the compound. The very small P_{A+M} found by Sutton, New and Bently[1] for diiodoacetylene has been interpreted by them as indicating a zero moment for the molecule. Weissberger and Sängewald[2] showed that diphenylacetylene has a small value of P_{A+M} and this they assumed to indicate zero polarity for the compound. Both groups of investigators conducted their experimental work at one temperature which introduces an uncertainty in their conclusions as this method does not distinguish between atomic and orientation polarization. With the point of establishing more definitely the structure of symmetrically disubstituted acetylenes the authors selected two dialkyl substituted compounds, the normal dibutyl and the normal diamyl.

The polarizations of these compounds were determined at 25°, one in heptane and the other

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[1] Sutton, New and Bently, *J. Chem. Soc.*, 652 (1933).

[2] Weissberger and Sängewald, *Z. physik. Chem.*, **20B**, 145 (1933).

in benzene. The polarization values for dibutylacetylene in heptane in seven measurements varied between 50.42 and 50.81, while those for diamylacetylene in benzene in nine measurements varied between 59.27 and 60.72, over very wide concentration ranges. Owing to the fact that the polarization of the solute is in both cases substantially independent of concentration it is sufficient in determining P_∞ at a series of temperatures to work with the pure compound only. Measurements of density and dielectric constant were made over a temperature range of 25 to 125°. The results are given in Table I.

Table I

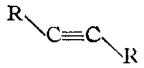
Dielectric Constants, Densities and Polarizations of Dialkyl Acetylenes

Temp., °C.	ϵ	d	P_2
A. Dibutylacetylene			
25	2.173	0.7642	50.81
50	2.136	.7443	50.98
75	2.099	.7235	51.19
100	2.062	.7024	51.42
125	2.025	.6815	51.62
B. Diamylacetylene			
25	2.171	0.7767	60.06
50	2.134	.7582	60.12
75	2.097	.7389	60.22
100	2.060	.7191	60.33
125	2.023	.6994	60.42

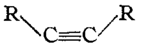
Table I shows that P_2 for the pure substances, which has been shown to be substantially the same as P_∞, instead of decreasing with rise in temperature actually increases. This increase of polarization with temperature is practically of the same magnitude as has been found for typically non-polar liquids such as heptane, benzene and decalin. With non-polar liquids the increase of polarization with temperature is due principally to a change in electronic polarization. The data show that the moments of symmetrical dialkyl acetylenes are no greater than those of the above-mentioned non-polar liquids, that is, practically zero. It is to be noted that the dielectric constants of the two pure acetylenes are less than that of benzene and this fact alone is strong evidence of the absence of a moment. The simplest structure consistent with zero moment is A.

$R{-}C{\equiv}C{-}R$

A



B



C

The presence of an appreciable portion of the acetylidene compound $R_2C{=}C$ is obviated. Considerations of symmetry make structure A more probable than structure B. If structure B exists, the existence of an isomer of the form C would seem likely. No such isomer is known.

Since P_M is zero the value of P_A can be determined by subtracting P_E from P_2. The value of P_E is obtained by extrapolating the value of molecular refraction to infinite wave length by the use of the equation

$$MR_\infty = \left(1 - \frac{\lambda_0^2}{\lambda^2}\right)\left(\frac{n^2 - 1}{n^2 + 2}\frac{M}{d}\right)$$

In the equation λ is the wave length corresponding to the index of refraction n, and λ_0 is the wave length corresponding to a characteristic frequency of vibration in the ultraviolet. The index of refraction was determined at 25° for the α, β and γ lines of hydrogen and the D line of sodium. By solving simultaneous equations it was not necessary to determine λ_0. Checks on the experimental work were obtained by calculating MR_∞ from the α and γ lines of hydrogen and from the β line of hydrogen with the D line of sodium. Table II gives the data on refractivity.

Table II

Index of Refraction and Molecular Refractivity at 25° C.

	n	MR	MR_∞	
A. Dibutylacetylene				
H_α	1.42879	46.583	H_α and H_γ	45.678
Na_D	1.43128	46.822	H_β and Na_D	45.646
H_β	1.43723	47.396		
H_γ	1.44165	47.798	Average	45.66
B. Diamylacetylene				
H_α	1.43552	55.899	H_α and H_γ	54.813
Na_D	1.43802	56.168	H_β and Na_D	54.785
H_β	1.44408	56.841		
H_γ	1.44853	57.335	Average	54.80

The value of P_A is thus found to be 5.15 (50.81–45.66) for dibutylacetylene and 5.26 (60.06–54.80) for diamylacetylene. These large values of P_A for hydrocarbons of the molecular weights 138 and 166, respectively, are undoubtedly associated with the high degree of unsaturation of the triple bond.

Experimental

The apparatus used for determining the dielectric constant was the heterodyne beat method type modified by using a radio broadcasting station in place of the stand oscillator. The point of zero beat was observed by noting the absence of distortion in the music or voice coming from the loud speaker of a radio receiving set. This method has been thoroughly tested with known compounds. On account of the geographical location of Notre Dame, station WGN of Chicago was selected for the work. For work above 25° a bath of Polarine lubricating oil was used as a heating medium instead of water. Temperature control was maintained to within ±0.01° with a mercury filled regulator.

Summary

1. The symmetrical dialkyl acetylenes have been shown to have zero moment.

2. The atomic polarization of these compounds has been determined and is seen to be somewhat higher than that of the more saturated hydrocarbons of the same molecular weight.

NOTRE DAME, INDIANA RECEIVED JANUARY 6, 1934

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Ionization Constant and Heat of Ionization of the Bisulfate Ion from Electromotive Force Measurements[1]

BY WALTER J. HAMER

Sulfuric acid is known to be a partially weak electrolyte. Several investigators by widely different methods have determined the extent to which the bisulfate ion dissociates, and the values of the dissociation constant obtained at 25° vary from 0.03 to 0.01. Part of this divergence depends upon whether or not corrections are made for interionic attraction. In 1926 Sherrill and Noyes[2] obtained 0.0115 at 25° from combined conductance and transference data of Noyes and Stewart[3] by taking into account the mobility and activity corrections which are given by the theory of interionic attraction developed by Milner and Debye and Hückel.[4] Since then, a method employing galvanic cells without liquid junctions has been developed for the determination of the ionization constants of weak electrolytes, and was applied to acetic acid solutions with a high degree of accuracy by Harned and Ehlers.[5] Their method with a slight modification for a uni-bivalent electrolyte has been employed in this research. This procedure possesses the advantage over previous methods in that it gives a determination of the constant from a single series of measurements. To extend the knowledge of this subject and to determine the heat of ionization of the bisulfate ion with accuracy, measurements were made at five-degree temperature intervals from 0 to 60°.

Discussion of the Method

The cell employed for the determination was

$$H_2 \mid NaHSO_4(m_1),\ Na_2SO_4(m_2),\ NaCl(m_3) \mid AgCl \mid Ag^+$$

which is seen to contain a sodium acid sulfate–sodium sulfate buffer mixture. The molalities were made nearly equal in order to give a one-one buffer mixture which is ideal experimentally and facilitates later calculations of hydrogen ion concentration. In this cell the hydrogen electrode is reversible to the hydrogen ion which is produced by the ionization of the bisulfate ion, and the silver–silver chloride electrode is reversible to the chloride ion.

The electromotive force of the cell in question is given by the well-known equation

$$E = E_0 - (RT/F)\ln m_{H}m_{Cl}\gamma_{H}\gamma_{Cl} \qquad (1)$$

The thermodynamic equation for the second dissociation of sulfuric acid is

$$K_2 = \frac{m_{H}m_{SO_4}\gamma_{H}\gamma_{SO_4}}{m_{HSO_4}\gamma_{HSO_4}} \qquad (2)$$

K_2 is the second dissociation constant, "m's" and "γ's" represent the molalities and activity coefficients, respectively, of the ionic species denoted by subscripts, and E_0 is the normal electrode potential of the silver–silver chloride electrode. We shall proceed upon the assumption that the dissociation of sulfuric acid into hydrogen and bisulfate ions is complete. Upon elimination of m_H in equations (1) and (2) and using the limiting law of Debye and Hückel with an additional linear term for the individual ionic activity coefficients

$$\frac{(E - E_0)F}{2.3026RT} + \log m_{Cl} + \log m_{HSO_4} - \log m_{SO_4} + 2A\sqrt{\mu} = -\log K_2 + 2\beta'\mu \qquad (3)$$

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[1] This contribution is part of an investigation of the thermodynamic properties of the electrodes and electrolyte of the lead accumulator. This work was made possible by a grant from the Naval Research Laboratory, Anacostia Station, Washington, D. C., and is published with permission of the Secretary of the Navy.

[2] Sherrill and Noyes, THIS JOURNAL, **48**, 1861 (1926).

[3] Noyes and Stewart, *ibid.*, **32**, 1133 (1910).

[4] Milner, *Phil. Mag.*, **23**, 551 (1912); **25**, 742 (1913); Debye and Hückel, *Physik. Z.*, **24**, 185, 305, 334 (1923).

[5] Harned and Ehlers, THIS JOURNAL, **54**, 1350 (1932).