the reaction with the metals to take place much more readily than with the halogens; and, if positive ions, we should expect the reverse.

As these experiments were performed without the use of a carrier gas, as has been used almost exclusively by previous investigators, and at a much lower total pressure, it is established that the active particles can be formed under these conditions.

Summary

Two new reactions of the transitory ethyl and methyl fragments formed in the thermal decomposition of lead tetraethyl and lead tetramethyl have been investigated.

They have been found to react with elementary sodium to form sodium ethyl and sodium methyl.

They have been found to react with carbon tetraiodide to form ethyl iodide and methyl iodide.

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The Absorption and Fluorescence Spectra of the Acid Sulfates of Quinine and Ten of its Derivatives in Water and Aqueous Sulfuric Acid Solution

BY LAWRENCE J. HEIDT AND GEORGE S. FORBES

The main purpose of this investigation was to determine accurately the absorption spectra of the bisulfates of quinine and its derivatives used by us in earlier work.[1,2,3] For comparison with that work, half our measurements were carried out in 0.9 molar sulfuric acid. In such a solution the loss of hydrogen ion due to the photochemical reaction can be neglected, as well as the accompanying change in the molar extinction coefficient, K, of the reactants.[1] Previous workers have plotted absorption curves of the acid salts of several of these compounds,[4] but little attention has been given to the effects of changing the groups attached to the quinoline nucleus particularly at positions four and six. Also the range of acidity covered has been small. That such effects do occur has been suggested by values of K determined throughout the spectrum for quinine[2] and at isolated wave lengths for the other compounds.[3]

The fluorescence spectra of these compounds was also studied to account for the low quantum yield (around 0.07) of the photochemical reaction with

(1) Forbes, Heidt and Boissonnas, THIS JOURNAL, **54**, 960 (1932).
(2) Forbes, Heidt and Brackett, *ibid.*, **55**, 588 (1933).
(3) Forbes and Heidt, *ibid.*, **55**, 2407 (1933).
(4) For data and a review of the literature see Hicks, *Australian J. Exptl. Biol. Med. Sci.*, **7**, 171 (1930).

dichromic acid. Many[5] have investigated, chiefly in the visible, the fluorescence spectrum of quinine. Except for cinchonine, cinchonidine, and quinidine,[5f] no similar studies have been made of its derivatives.

Experimental

Materials were purified as previously described.[1,3]

For the work on absorption, we used a null photographic method involving the Judd-Lewis comparison quartz sectorphotometer of Hilger. The two sectors of the instrument were recalibrated as follows. The center of a 40-watt frosted tungsten lamp (110 volts d. c.) was placed at the front focus of the photometer. The current through the lamp was held constant by means of an ammeter and rheostat placed in its circuit. The lamp housing had a chimney. A surface thermopile connected to a high sensitivity galvanometer with an illuminated scale five meters distant was substituted for the absorption cells. It just intercepted the whole of the parallel beam from the given sector. Drafts and stray light were eliminated by placing a paper cone in front of the pile and by covering the lamp and pile system with black cloth. A shutter was placed between the pile and the sector. After operating the lamp for five minutes, the galvanometer deflection was noted with the sector set at 0°. This was repeated at ten-minute intervals during the calibration. A plot of these deflections against time gave the zero correction at any time, t. Noting the time, the average of at least five deflections for each setting of the sector was taken, working out at 5° intervals in both directions from 45°. Calibration curves were then made for each of the two sectors, plotting $-\log (I/I_0)$, *i. e.*, log of the ratio of the galvanometer deflection at a given angle to the deflection at 90° for the same sector after appropriate zero-point corrections, against angular settings, Θ, of the sector. With the aid of a set of Scheibe absorption cells, the logs of whose lengths varied successively by one-tenth, a table was then constructed in which for given concentrations of solute (0.001 and 0.0001 molar used in this work) and given cells, Θ was varied so that $\log K$ varied by increments of one-tenth irrespective of the total magnitude of K. This appears to be a novel and useful variation of the traditional method of obtaining absorption curves. Lengths of exposure for given angular settings were such that at the null point the blackening on the photographic plate was always the same; *i. e.*, $\log^{-1} (I_0/I)$ equaled the relative time of exposure (with our light source the actual time in seconds). Wratten and Wainwright, M., and Cramer contrast plates were used for work in the visible and ultraviolet, respectively. Because of the greater percentage accuracy in timing the exposure, and the more rapid change in photographic density about the null point for large values of $\log (I_0/I)$, small values of Θ, the instrument was most sensitive about values of $\log (I_0/I) = 1.5$. Hence the sectors were used at large values of Θ only in the steepest parts of the absorption curves.

The spectroscope had been originally constructed by Professor P. A. Leighton.[6] It consisted of an adjustable rectangular pupil 0.5 cm. high, two fused quartz lenses (focal length 66 cm. for λ 313 mμ) 4 cm. in diameter, stopped down to 2 cm.; a fused quartz prism 4 cm. on a side and 3 cm. high; and a light-tight plate holder mounted flush against an exit slit 0.5 cm. high and 25.4 cm. long. The holder held a plate 10.2 × 25.4 cm. and had a vertical adjustment enabling one to take sixteen separate exposures on a single plate. The plate holder and the exit slit, mounted in a light-tight black box, could be slid in and out of a similar box containing the pupil, lenses and prism. The boxes were adjusted so that the focal plane of the back lens coincided with the sensi-

(5) See for example: (a) Perrin, *Compt. rend.*, **178**, 1978 (1924); (b) **183**, 329 (1926); (c) Dhar, *Z. anorg. allgem. Chem.*, **155**, 303 (1926); (d) Mather and Bhatnagar, *Indian J. Physics*, **3**, 37 (1928); (e) West, Muller and Jette, *Proc. Roy. Soc.*, **A121**, 294 (1928); (f) Andant, *Compt. rend.*, **189**, 98 (1929); (g) Dutt, *J. Indian Chem. Soc.*, **7**, 505 (1930); (h) Colombier, *Ann. fals.*, **24**, 89 (1931).

(6) Leighton and Forbes, THIS JOURNAL, **51**, 3553 (1929).

tized surface of the plate. The spectrograms now showed adequate definition. On the focal plane, the distance between the mercury lines λ 620 and 238 mμ was 16.1 cm.

A spark between high tungsten steel electrodes, 0.7 cm. in diameter and 0.6 cm. apart, was patterned after that used by Dr. F. L. Gates.[7] The electrodes were tapered flat on two sides to 3 mm. at the ends. To facilitate starting and stopping the spark, the atmosphere between the electrodes was kept ionized by a small gas flame surrounding the lower electrode. Intensity was maintained constant by placing a 1-mm. spark gap in series. The spark circuit, consuming about 4 kw., was substantially as described by Forbes and Brackett.[8] The center of the spark was placed at the common focal point of the front lenses of the photometer, located (by trial) by placing a light at the opposite end of the instrument. Other experimental details followed those given in the directions accompanying the sectorphotometer. Measurements were made at 23 ± 2°. At the beginning and end of each set of observations on a plate, a comparison spectrogram was always taken without any cells in the path of the parallel beams. If the halves of the comparison spectrogram were not identical, the plate was discarded. In addition each plate recorded seven spectrograms of the acid solution of the given compound, and seven spectrograms yielding the same values of log K in the corresponding water solution. We give the absorption curves of the compounds in acid only. In water the curves had nearly the same form but were shifted away from the red by about 200 cm.$^{-1}$. In the figures, open and black circles indicate, respectively, values by the null photographic method and by spectroradiometer with thermopile. The initial ordinate, log K, 1.4, is located for each and every curve at the extended line just below its left extremity. Wave numbers, ν, and wave lengths, λ, are plotted as abscissas.

Fluorescence spectra were determined using a Féry reflecting spectrograph (by Hilger) kindly lent by the Wolcott Gibbs Memorial Laboratory. It had a curved quartz prism and a dispersion of 20 cm. from λ 500 to 219 mμ. The light source was focused on the vertical slit by means of an adjustable cylindrical lens suitably attached to the instrument. Spectra were ordinarily photographed on Agfa portrait film. Duplitized x-ray films are much better. On each film, the lines of an iron arc were photographed as a standard of reference.

The fluorescence tube, B (capacity 40 cc.), was made from 2-cm. Pyrex tubing and had two horns blackened on the outside to act as light traps. The windows were made of optically clear fused quartz (0.05 cm. thick) sealed on with de Khotinsky cement. To avoid evaporation, the open ends were corked. Monochromatic light (λ was in general 366 mμ) was obtained from a mercury vapor lamp[9a] by means of a monochromator.[9b] The focal length of the back lens was 60 cm. One window of B was placed flush against the exit slit (0.02 cm. × 0.5 cm.) so that the slightly diverging beam almost grazed the other window of B perpendicular to A.

The work was carried out in a dark room and extreme precautions were taken against stray light. With water in B, no trace of photographic blackening could be observed after exposures as long as twenty-four hours. Further, the exciting spectral line was not visible upon any of the films. Concentrations of excited molecules were uniform (compare Perrin)[5a] except for cinchonine and cinchonidine, as the incident radiation intensity and the extinction per cm. of solution were held constant. Concentrations were not so great as to reabsorb unduly the ultraviolet component of the fluorescence.

Data and Discussion

The absorption curves of compounds having groups of various sizes at position six of the quinoline nucleus, shown in Fig. 1, are on the whole

(7) Gates, *J. Gen. Physiol.*, **14**, 37 (1930).

(8) Forbes and Brackett, THIS JOURNAL, **53**, 3973 (1931).

(9) (a) Forbes and Heidt, *ibid.*, **53**, 3973 (1931); (b) Villars, *ibid.*, **49**, 326 (1927).

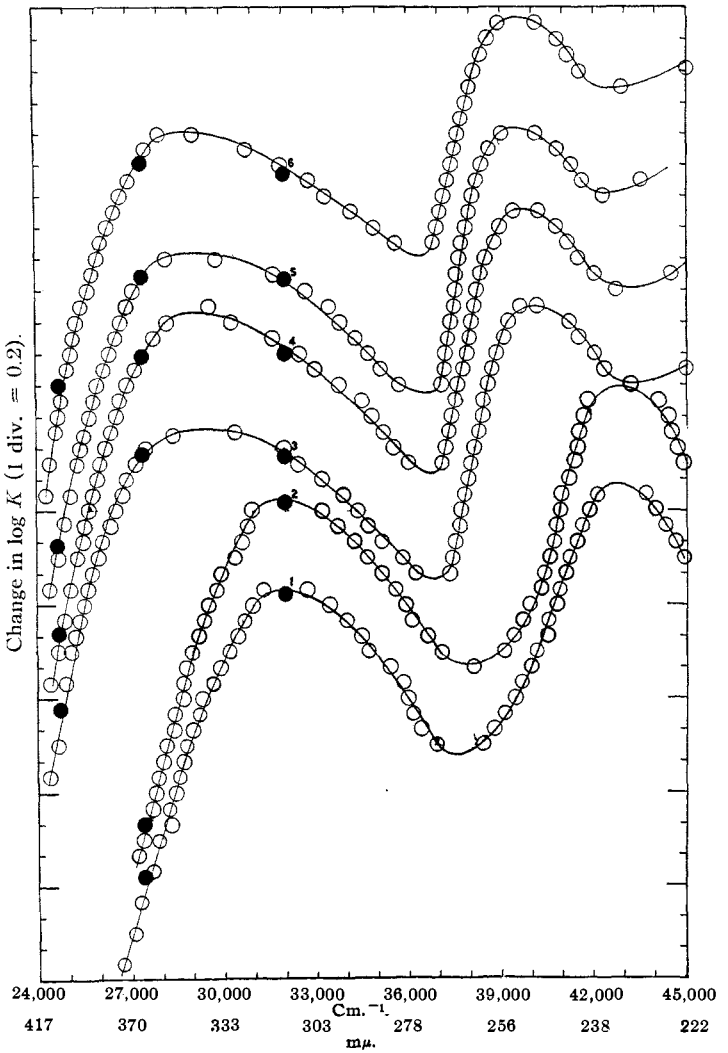

Fig. 1.

Curve	Compound	Group attached at position six of quinoline nucleus	Maximum 1 log K_1	ν_1	Minimum 1 log K_2	ν_2	Maximum 2 log K_3	ν_3	Minimum 2 log K_4	ν_4
1	Cinchonidine	Hydrogen	3.90	32,000	2.85	37,500	4.55	42,800		
2	Cinchonine	Hydrogen	3.90	32,000	2.80	38,000	4.60	42,800		
3	Hydrocupreine	Hydroxyl	3.70	29,200	2.75	36,800	4.50	40,000	4.00	43,500
4	Optochin	Ethoxyl	3.90	29,000	2.85	36,700	4.50	39,700	4.00	43,200
5	Eucupin	Isoamoxyl	3.60	29,000	2.75	36,500	4.45	39,400	4.00	42,400
6	Vuzin	Isooctoxyl	3.80	29,000	3.00	36,500	4.55	39,500	4.10	42,500

Curve	Compound	ν_0 at log K, 1.5	ν_1^* at log K_1	ν_2^* at log K_2	ν_4^* at log K_4
1	Cinchonidine	26,700	40,900	28,800	
2	Cinchonine	27,100	41,000	28,900	
3	Hydrocupreine	24,400	38,300	25,700	38,600
4	Optochin	24,400	38,100	25,900	38,300
5	Eucupin	24,400	37,800	25,900	38,100
6	Vuzin	24,300	37,700	26,000	38,000

similar. They shift slightly toward smaller wave numbers and the absorption maxima become broader as the size of the attached group increases.

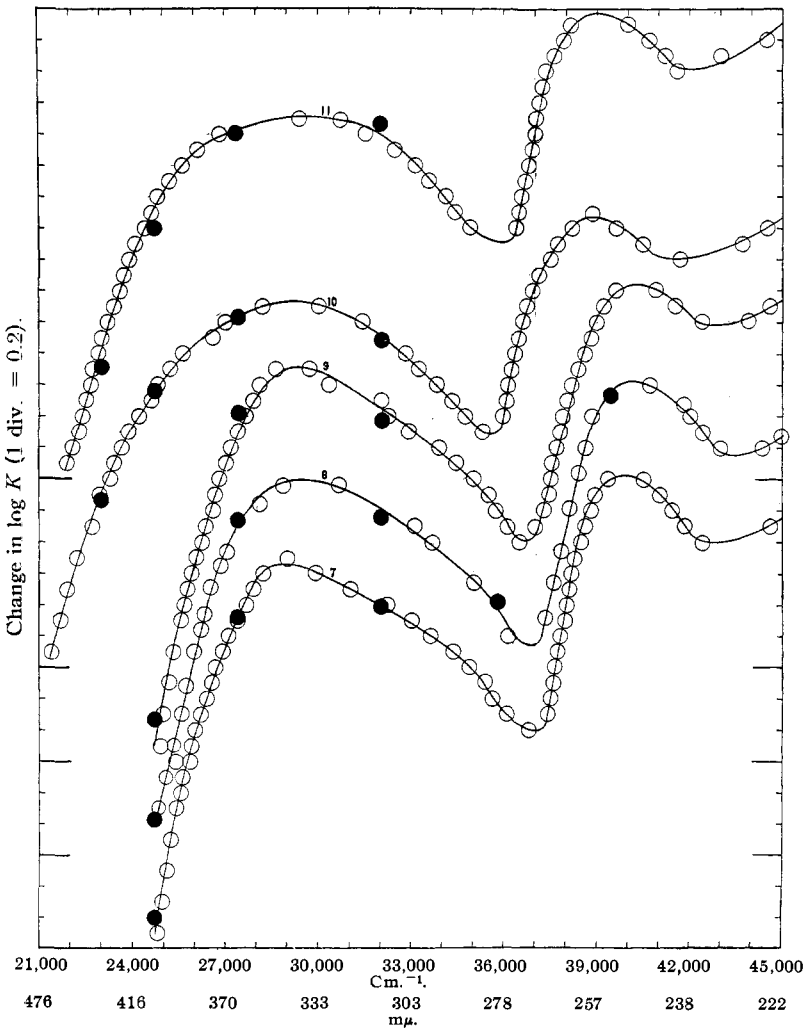

Fig. 2.

Curve	Compound	Maximum 1 Log K_1	ν_1	Minimum 1 Log K_2	ν_2	Maximum 2 Log K_3	ν_3	Minimum 2 Log K_4	ν_4
7	Quinidine	3.85	29,000	2.80	37,000	4.40	40.000	4.00	42,800
8	Quinine	3.80	29,400	2.75	37,000	4.40	40,000	4.00	43,000
9	Hydroquinine	3.90	29,400	2.80	36,500	4.45	40,300	4.20	42,800
10	Quinicine	3.70	29,000	2.90	36,000	4.35	39,000	4.00	41,700
11	Quininic acid	3.70	29,400	2.90	36,000	4.35	39,000	4.00	42,000

Curve	Compound	ν_0 at log K, 1.5	ν_1^* at log K_1	ν_2^* at log K_2	ν_4^* at log K_4
7	Quinidine	24,700	38,200	26,000	38,400
8	Quinine	24,700	38,400	26,100	38,500
9	Hydroquinine	24,700	38,400	26,200	38,900
10	Quinicine	21,400	36,900	23,800	37,400
11	Quininic acid	21,900	37,100	24,200	37,500

Curves for cinchonine and its optical isomer, cinchonidine, are similar. The same holds for quinine and quinidine. Absorption curves of the corresponding bases, of their hydrochlorides, and of their normal sulfates in water and in alcohol are similarly related.[4,10] Our expectation[3] that log K at λ 313 mμ (ν = 32,100 cm.$^{-1}$) would differ little from log K at the first absorption maximum, is thus fulfilled. Hence, differences in the quantum yield, ϕ_q, of the reduction of chromate by quinine or its derivatives, Q^*, excited by absorption of light (λ 313 mμ) are not due to shifts of the absorption patterns with respect to this wave length. Furthermore, for quinine, optochin, eucupin, and vuzin, ϕ_q is 0.025 $\pm$ 0.005 at λ 405 mμ, other variables remaining fixed, while K changes four-fold. This wave length still falls upon the corresponding steep portions of the curves. Our assumption[3] that ϕ_q for these compounds is independent of K at λ 313 mμ, thus receives additional support.

In Fig. 2 are given the absorption curves of the compounds used to determine the group in quinine largely responsible for the photochemical reduction of chromate.[3] Again the patterns are similar, suggesting that the quinoline group is the determining factor in absorption. The shift toward the visible and the broadening of absorption maxima are even greater than in Fig. 1. These enhanced effects are probably due to the supposed enolic group of quinicine replacing the hydroxyl group of quinine and the carboxyl group of quininic acid replacing both the hydroxyl and quinuclidine groups of quinine.[3] As expected, the enolic group produces the greater effect. The minor part played in light absorption by changes in the quinuclidine groups is brought out strikingly in the approximate identity of the curves for quinine, its optical isomer, quinidine, and its hydrogenated homolog, hydroquinine. This is again in agreement with the work of others on these bases or other salts of them.[4,10] Figure 2 again verifies our assumption that variations of ϕ_q at λ 313 mμ, other variables fixed, are not due to shifts of the absorption patterns with respect to this wave length.

The total area under the curves between ν_0 and ν_2, *i. e.*, $\int_0^{\log K \text{ at } \nu} d(\log K) \int_{\nu_0}^{\nu_2} d\nu$ is approximately twice the similar area between the first and second minimum, *i. e.*, $\int_0^{\log K \text{ at } \nu} d(\log K) \int_{\nu_2}^{\nu_4} d\nu$. Also $(\nu_2 - \nu_1)/(\nu_1 - \nu_2^*) = 2 \pm 0.1$ and $(\nu_4 - \nu_3)/(\nu_3 - \nu_4^*) = 2 \pm 0.1$, evidence the constant asymmetry about the broadening maxima.

Physically the structure of the curves suggests three electronic levels with their accompanying vibrational and rotational levels—perturbed by kinetic and electrostatic effects—producing each broadened continuum. Absorption due to electron level (1) appears to start at the long wave

(10) "International Critical Tables," Vol. V, pp. 369–371.

length limit of the curves, and increases very rapidly. That due to electronic level (2), because of its steep initial slope and its similarity with (1), probably begins near the first minimum, ν_2, and again increases rapidly. That due to the third electronic level (3) might at first sight appear to start near the second minimum, ν_4, and increases slowly with ν. The fact that patterns due to levels (1) and (2) are very similar (including initial slopes) suggests that corresponding vibrational and rotational levels are associated with these electronic levels. If this is the case, probably neither electronic level leads directly to dissociation or rearrangement of the absorbing molecules, as was verified experimentally, at least in the case of quinine.[3] However, the different character of the part associated with (3) suggests a different potential energy curve which might lead directly to dissociation or rearrangement. Absorption of light in the regions (1) and (2), however, may produce chemical reaction directly because of the overlapping of (3) into this region or indirectly through a distribution of absorbed energy, in accord with the known rearrangement of quinine on pyrolysis into quinicine.[11] The finite probability of such a distribution of energy may depend largely on slight changes in the structure of the molecule as is implied in the differences of ϕ_q for cinchonine and quinine under similar conditions.

With a recording photometer kindly lent by Professor G. B. Kistiakowsky, densitometer records were made of ten of the original fluorescence spectrograms. None of these gave any evidence of structure. All maxima were very broad and flat. For lack of sensitometry data upon the films employed, it would be pointless to record the wave numbers of the maximum ordinates.

The fluorescence spectra of the compounds given in Table I exhibit no well-defined differences. As the film was not panchromatic, the uniformity in $\nu_{min.}$, and the non-appearance of fluorescence spectra in the case of quininic acid and hydrocupreine may be due to the sensitivity factor. Identical spectrograms were obtained for quinine excited by light of λ 366 mμ and 313 mμ. The spectra of cinchonine in acid produced identical blackening on both Agfa portrait films and on "duplitized" x-ray films. The results of Table I are in general agreement with Andant,[5f] who found the fluorescence spectra of quinine and quinidine to be identical. Contrary to his findings our photographs indicate that hydrogen substituted for methoxyl at position six of the quinoline nucleus does not shift the fluorescence spectra to the ultraviolet either in going from quinine to cinchonine or from quinidine to cinchonidine. Andant, although he presents no data, finds the spectrum shifted to the visible on salt formation. If this shift approaches the same minimum wave number for all the alkaloids studied except for hydrocupreine and quininic acid, our disagreement with Andant disappears.

(11) Heidelberger and Jacobs, THIS JOURNAL, 41, 817 (1919).

TABLE I

EXCITING RADIATION $\simeq 10^{17}$ QUANTA PER MIN. OF λ 366 mμ. TEMP., 25 ± 2°

Compound	Molar concn.	Extinction per cm. at λ 366 mμ	[H_2SO_4]	Time of exposure in min.	Fluorescence limits, $\nu_{min.}$	$\nu_{max.}$	Visible fluorescence
Cinchonine	0.001	0.063	0.0	1110	19,800	25,600	Light blue which
			.9	330	20,600	24,000	disappeared after prolonged exposure
Cinchonidine	.001	.117	.0	930	20,900	24,000	
			.9	925	20,600	24,100	
Hydrocupreine	.00025	.916	.0	655	None	None	Very faint pink
			.9	1200	None	None	Very faint pink
Quininic acid	.00025	1.00	.0				Light yellow
			.9	600	None	None	Light yellow
Quinicine	.00025	1.08	.0				Light blue
			.9	1440	19,800	23,600	Light blue
Quinine	.00025	0.86	.0	180	20,300	25,200	Blue
			.9	600	19,000	25,600	Blue
Quinidine	.00025	.83	.0				Blue
			.9	1280	19,500	25,200	Blue
Hydroquinine			.0				Blue
			.9				Blue
Optochin	.00025	.945	.0				Blue
			.9	1025	18,500	25,600	Blue
Eucupin			.0				Blue
			.9				Blue
Vuzin	.00025	1.04	.0	1430	19,000	24,900	Blue
			.9	1935	19,500	24,700	Blue

Dutt[5g] found that quinine and other compounds commonly fluorescent, did not fluoresce visibly in sunlight after being subjected to extreme purification by repeated precipitation by ammonia from dilute alcohol. They appeared to regain their ability to fluoresce only on exposure to air. In this connection, it should be noted that, although our anhydrous quinine showed no visible fluorescence in absolute alcohol on exposure in Pyrex to the total radiation of a Uviarc, the sulfuric acid solution did.

The uniformly similar character of the fluorescence spectra of these alkaloids suggests the same structure for the fluorescing unit. As the absorption spectra similarly showed the quinoline group to be the absorbing unit, it may be inferred that a large part of the absorbed energy is re-emitted before it has a chance to distribute itself into other parts of the molecule. This may be taken to account in part for the low values of ϕ_q.

We gratefully acknowledge grants from the Warren and du Pont funds for the purchase of the Judd-Lewis sectorphotometer and photographic supplies, respectively.

Summary

Absorption spectra (from 20,000 to 45,000 $cm.^{-1}$) of the bisulfates of (1) cinchonine, cinchonidine, hydrocupreine, hydroquinine, optochin,

eucupin and vuzin and (2) quinine, quinidine, quinicine and quininic acid in aqueous solution all shift about 200 cm.$^{-1}$, to smaller wave numbers when 0.9 molar sulfuric acid is substituted as a solvent.

As the size of the group attached to position six of the quinoline nucleus of the alkaloids (1) increases from hydrogen to isooctoxyl, respectively, the absorption maxima broaden as the patterns shift toward smaller wave numbers. This also occurs when the secondary hydroxyl group of quinine at position four is replaced by a carbonyl group (quinicine) or by a carboxyl group (quininic acid).

The fluorescence spectra of most of these compounds excited by monochromatic radiation of λ 366 mμ under comparable conditions in water and in sulfuric acid have been photographed and the spectrograms analyzed using a recording densitometer. No evidence of structure was observed, and all spectrograms were substantially identical.

These results have been interpreted to account in part for the low values of the quantum yield of the photochemical reduction of chromate by these compounds when excited by absorbed light.

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The Compressibility of Solutions. I. The Apparent Molal Compressibility of Strong Electrolytes

BY FRANK T. GUCKER, JR.

Introduction

For many years a host of workers have investigated the conductivity and colligative properties of solutions of electrolytes, and from these studies we have developed our modern ideas of such solutions. Quite recently, the study of other properties of these same solutions has disclosed several important generalizations which must be considered in completing our theories of strong electrolytes. Randall and his co-workers[1] have showed that the apparent molal heat capacity of such solutions is a linear function of the square root of the molality over a wide range of concentration. Masson[2] has found that the apparent molal volume of solutions of strong electrolytes is also a linear function of the square root of the concentration. Scott and Geffcken[3] have verified this generalization in the case of many salts.

It seemed of interest to study the existing compressibility data, to see if the apparent molal compressibility of strong electrolytes showed the

(1) Randall and Ramage, THIS JOURNAL, **49**, 93 (1927); Randall and Rossini, *ibid.*, **51**, 323 (1929).
(2) Masson, *Phil. Mag.*, [7] **8**, 218 (1929).
(3) Scott, *J. Phys. Chem.*, **35**, 2315, 3379 (1931); *ibid.*, **37**, 1022 (1932); Geffcken, *Z. physik. Chem.*, **A155**, 1 (1931).