[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Rates and Temperature Coefficients in the Hydrolysis of some Aliphatic Esters with a Cation Exchange Resin as the Catalyst[1]

BY VERNON C. HASKELL AND LOUIS P. HAMMETT

It has been noted recently[2] that acidic cation exchangers such as sulfonated coal and resinous exchangers containing sulfonic acid groups are effective as catalysts for various acid-catalyzed reactions. The practical advantages of an acidic catalyst which can be separated quickly and easily from a reactive solution are obvious. From the theoretical point of view this example of heterogeneous catalysis in which the number of active sites on the catalyst can be measured with some certainty possesses considerable interest. A comparison of the kinetics of a reaction catalyzed by a solid acid and by an acid in solution should for instance provide useful information about the mechanism of the heterogeneous process.

The acid-catalyzed hydrolysis of esters in 70% acetone, studied previously by others,[3] was selected for this work; the kinetics of the homogeneous reaction are of the first order in ester concentration, the reaction is easy to follow by titrating the carboxylic acid with standard alkali solution, and the rates are of conveniently measurable magnitude at room temperature. The solid-catalyzed reaction has an advantage that the catalyst acid need not be titrated if the carboxylic acid can be rinsed from the solid rapidly.

Experimental

The esters used in the rate experiments were fractionated in a thirty-inch column of glass helices, the fractions retained in each case boiling in a range of not more than 0.2°. The following are the esters used with their sources, boiling points (uncor.) at atmospheric pressure, and saponification analyses: methyl acetate, 56.3°, 100.2%; ethyl acetate, Mallinckrodt, 76.6°, 99.5%; ethyl *n*-butyrate, Eimer and Amend, 121.0°, 100.5%; ethyl *n*-caproate, Eastman Kodak, 165.4°, 99.4%. U.S.P. grade acetone was boiled with alkaline permanganate and was fractionated in the above column, the fraction retained boiling over a range of not more than 0.2°.

Sulfonated coal and two synthetic resin cation exchangers were examined as possible catalysts. The resinous exchanger selected[4] was chosen not for its efficiency as a catalyst but because its exchange capacity could be measured within limits of ±0.3% by a simple titration with standard alkali. In contrast the attempts to titrate the other exchangers gave end-points which were neither sharp nor reproducible. Moreover the selected exchanger had a high exchange capacity (3.95 to 4.32 meq. per g. depending on the moisture content) and was available in the form of spherical particles which could be separated into narrow fractions with standard sieves giving samples of easily calculated external area. Fractions taken between 40 and 45 mesh sieves (average diameter 0.38 mm.) and between 80 and 100 mesh sieves (average diameter 0.16 mm.) were used in subsequent rate experiments.

Rate experiments were carried out in thermoregulated water-baths, the temperatures being 12.5, 25.0 and 37.5° with an estimated ±0.02° error. The 25.0 and 37.5° baths were of the conventional type. The 12.5° bath was as described elsewhere.[5]

The solid-catalyzed reactions were done with individual samples of acidic cation exchanger and proportionate volumes of reacting solution in sealed tubes of 12-mm. Pyrex tubing 10 to 15 cm. long. A shaker was designed to provide continuous agitation by tumbling the tubes over at about 30 r. p. m. A study of the effect of agitation showed that with this degree of agitation the rate of hydrolysis of methyl acetate was insensitive to the shaking rate.

Parallel experiments were performed with hydrochloric acid and the acidic cation exchanger respectively as catalysts. In the solid-catalyzed runs, six portions of exchanger weighing between 0.3 and 0.4 g. were delivered into the sample tubes described above. A reaction mixture was prepared from 70 ml. of acetone, 2 ml. of ester (except that 4 ml. of ethyl *n*-caproate was used) added from a volumetric pipet which was calibrated for each ester, and distilled water to make 100 ml. of solution. After agitation the solution was measured from a 10-ml. buret into the sample tubes in the proportion of 10 ml. of liquid per gram of catalyst. The tubes were immersed in ice water, sealed, and introduced into the shaker in the water-bath, the instant of introduction into the bath being taken as zero time. The tubes were broken at appropriate time intervals, the solid was separated by suction filtration through glass wool, and was rinsed with 75 to 100 ml. of distilled water over a period of about five minutes, and the solution with rinsings was analyzed for acid. Tests with acetic acid solutions showed that such rinsing recovered 99.8% of the acid. With the other acids, the reproducibility of the results was taken as evidence of the adequacy of the rinsing process. A 10-ml. buret was used for titration of the acid produced by the reaction and a correction was applied for the amount of base required to achieve a slightly pink shade with phenolphthalein in distilled water.

Measurements of exchange capacity were obtained from samples of catalyst which had been used in the rate experiment. After the rinse with distilled water the sample of exchange resin was transferred to an erlenmeyer flask and was mixed with 25 ml. of water and about 2 g. of solid sodium chloride. The acid was titrated to a phenolphthalein end-point with standard sodium hydroxide. The addition of an excess of sodium hydroxide and back-titration with standard hydrochloric acid gave agreeing results. The exchange capacity of the resin was the same before and after use as catalyst.

The experiments with hydrochloric acid as the catalyst were performed in 50 or 100 ml. volumetric flasks having glass stoppers. The reaction mixture was made up from 70 ml. of purified acetone, 10.00 ml. of 4.405 *N* hydrochloric acid and 2 ml. of ester (or 4 ml. of ethyl *n*-caproate) and distilled water to the 100-ml. mark. These were made up at 25° and were then transferred to the thermostat having the temperature desired. The change in

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(1) Dissertation submitted by Vernon Charles Haskell in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University, New York City, 1948.

(2) (a) Dierichs Report PB 866, Office of Technical Services, Dept. of Commerce, Washington, 1945; (b) Sussman, *Ind. Eng. Chem.*, **38**, 1228 (1946).

(3) (a) Davies and Evans, *J. Chem. Soc.*, 339 (1940); (b) Smith and Steele, THIS JOURNAL, **63**, 3466 (1941).

(4) Amberlite IR-120, kindly supplied by the Resinous Products and Chemical Co. This is reported (*Chem. Eng. News*, **26**, 1925 (1948)) to be a nuclear sulfonic acid cation exchange resin in bead form of high capacity and chemical stability.

(5) Price and Hammett, THIS JOURNAL, **63**, 2389 (1941).

volume was noted and the correction for change in concentration applied. The instant of addition of ester was taken as zero time but the initial point was not used except in experiments at 25°. In Fig. 1 the result of this technique is shown. The line for the hydrogen chloride-catalyzed hydrolysis of methyl acetate does not go through the origin. This does not affect the value of the specific rate which is obtained from the slope of the line.

Calculations

The values of k', the specific rate of the hydrolysis, were obtained by least squares methods from the slope of the plot of $\ln a/(a - x)$ against time, using points between zero and half-complete reaction. Here a is the concentration of organic acid which would be obtained if the reaction were complete, calculated from the composition of the original reaction mixture, and x is the concentration at time t. In the region used for the calculation these plots were linear within the precision of the measurements for both resin and hydrogen chloride-catalyzed reactions.

The k' values were approximately proportional to the concentration of catalyst acid in the homogeneous reaction; they were found to be very closely proportional to the ratio of quantity of resin to volume of solution in the heterogeneous one. Therefore a rate constant k was calculated in the former case by dividing k' by the concentration of catalyst acid, and in the latter case by dividing k' by the ratio of the number of moles of exchangeable acid in the resin to the volume of the solution. Since the k values thus obtained depended somewhat on the concentration of hydrochloric acid and on the initial concentration of ester the same concentration of a given ester was used in both homogeneous and heterogeneous reactions and a correction was applied for the small difference in acid concentrations between the two systems.

The energies of activation E were calculated using the equation

$$E = 2.303\ R\ \frac{T_1 T_2}{T_1 - T_2} \log \frac{k_1}{k_2} \qquad (2)$$

k_1 being the rate constant at temperature T_1.

Relative entropies of activation were obtained from the expression[6]

$$\Delta \Delta S^{\ddagger} = 2.303\ R\ \frac{\Delta (T \log k_r/k_a)}{\Delta T} \qquad (3)$$

k_r and k_a being rate constants for the same ester with the resinous catalyst and hydrochloric acid respectively at temperature T.

Results

The effect of agitation on the resin-catalyzed hydrolysis of methyl acetate in 70% acetone was studied by subjecting four similar samples of heterogeneous reaction mixture to different degrees of agitation. The results are given in Table I. The time of reaction was five hours. The relatively small difference between the amounts of acid production in the third and fourth samples showed that the limiting rate of reaction was being approached.

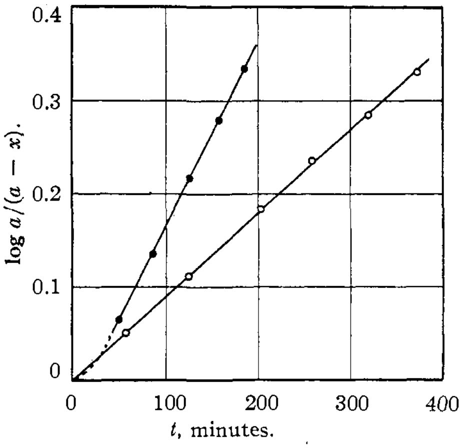

Fig. 1.—Hydrolysis of methyl acetate in 70% acetone at 37.5°: ● catalyst: 0.4350 N HCl (started at 25°, then transferred to 37.5° bath); ○ catalyst: 1.000 g. resin (4.30 meg. H_3O^+/g.) in 10.33 ml. of solution.

TABLE I

THE EFFECT OF AGITATION IN THE HYDROLYSIS OF METHYL ACETATE WITH AN ACIDIC EXCHANGE RESIN AS THE CATALYST

Sample	n (Half-minute shaking periods per hour)	Vol. of NaOH (per g. catalyst)
1	0.2	9.50
2	1	14.72
3	4	16.08
4	120 (continuous shaking)	17.02

The effect of varying the ratio of exchange resin to solution was studied in order to determine the order of the reaction with respect to the solid catalyst. Six samples of resin were weighed and were delivered into separate glass tubes. A solution of ethyl acetate in 70% acetone was prepared and was added to the samples of exchange resin in such proportions that the weight of resin per unit volume of solution varied regularly. The sample tubes were sealed, introduced into the 25° bath

TABLE II

THE EFFECT OF WT. RESIN/VOL. SOLUTION ON THE SPECIFIC RATE OF HYDROLYSIS OF ETHYL ACETATE IN 70% ACETONE AT 25°

Exchange capacity of resin: 4.23 meq. H_3O^+/g. Calculated titer for complete reaction of 10 ml. solution: a = 34.38 ml. of 0.05877 N NaOH solution. Blank on 100 ml. distilled H_2O, 0.06 ml.

Wt. resin, g. W	Vol. soln., ml. V	Vol. NaOH, ml.	$\log \frac{a}{a - x}$	$10^5 k'V/W$
0.122	3.67	2.30	0.0850	6.48
.196	2.94	3.36	.1718	6.53
.2885	2.88	4.48	.2560	6.49
.404	3.03	5.69	.3376	6.41
.521	3.13	6.80	.4274	6.50
.597	2.985	7.20	.5168	6.55

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[6] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 115–119.

and were shaken continuously for 1515 minutes. Titration of the acid formed and substitution of the results into the integrated first order rate equation gave the data of Table II.

These results indicate that the specific rate of the resin-catalyzed reaction is proportional to the "concentration" of resin.

Preliminary experiments were performed to elucidate the effect of surface area of the catalyst resin on the rate of ester hydrolysis. For equal weights of samples the resin passing between 80 and 100 mesh sieves had 2.4 times the geometrical area ($4\pi r^2$) of the 40 to 45 mesh material. The rate constants obtained with the same liquid mixture of a given ester were as shown in Table III.

TABLE III

THE EFFECT OF PARTICLE SIZE ON THE RATE OF THE EXCHANGER-CATALYZED HYDROLYSIS OF ESTERS

	10^6k		
Ester	40-45 mesh	80-100 mesh	% Difference
Ethyl acetate	14.8	15.4	+4.1
Ethyl *n*-butyrate	2.27	2.42	+6.3
Ethyl *n*-caproate	0.74	0.77	+4.4

Subsequent rate experiments were done with 40 to 45 mesh particles only.

Figure 1 is a graph of data from two representative rate experiments. The slopes of the best straight lines obtained by least squares calculation were 1.98×10^{-3} and 8.86×10^{-4} for the hydrogen chloride- and resin-catalyzed reactions, respectively, and the corresponding rate constants were 1.75×10^{-4} l. mol.$^{-1}$ sec.$^{-1}$ and 8.18×10^{-5} l. mol.$^{-1}$ sec.$^{-1}$.

The rate data obtained at 25° are summarized in Table IV. The units for the k values of Tables IV and V are l. mol.$^{-1}$ sec.$^{-1}$. Each rate experiment used in calculating catalyst efficiency and heats of activation was performed in duplicate.

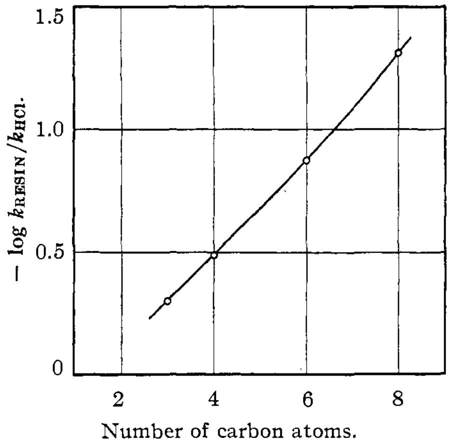

Fig. 2.—Efficiency of exchange resin compared with HCl as a catalyst, as a function of the chain length of the ester hydrolyzed in 70% acetone. Points in increasing order are for methyl acetate, ethyl acetate, ethyl *n*-butyrate and ethyl *n*-caproate.

TABLE IV

RATE CONSTANTS AT 25° FOR HYDROGEN CHLORIDE AND RESIN-CATALYZED HYDROLYSIS OF ESTERS

c_{HCl}: 0.4405 mol./l.

Ester	c_{ester}, mol./l	$k_{\text{HCl}} \times 10^5$	$k_{\text{HCl}} \times 10^5$ (cor.)^a	$k_{\text{Resin}} \times 10^5$	$\frac{k_{\text{Resin}}}{k_{\text{HCl}}}$
Methyl acetate	0.2483	5.45	5.41	2.70	
		5.44	5.40	2.74	0.502
Ethyl acetate	0.2020	4.61	4.58	1.49	
		4.66	4.63	1.51	0.326
Ethyl *n*-butyrate	0.1504	1.92	1.91	0.255	
		1.91	1.90	0.256	0.134
Ethyl *n*-caproate	0.2401	1.53	1.52	0.0741	
		1.53	1.52	0.0749	0.0490

^{a} The correction was necessary because the acidity of the hydrogen chloride-catalyzed experiments was 6% higher than that of the resin-catalyzed experiments. A 16% decrease in c_{HCl} lowered the rate constant for the hydrolysis of methyl acetate 2.2%. When account is taken of the moisture content of the exchange resin the concentration of water in the reaction mixture containing resin is greater than that in the reaction mixture containing hydrochloric acid by a factor of 1.08. No correction was applied. Because of this and because of possible medium effects associated with the solid catalyst more significance is attached to the variations of the k-ratios with the size of the ester molecules than to the actual values of the k-ratios.

Figure 2 shows the variation of the efficiency of the solid catalyst with the length of the ester molecule.

Methyl acetate and ethyl *n*-butyrate were hydrolyzed at 37.5° and at 12.5° and the heats and entropies of activation were calculated. The results are shown in Table V.

TABLE V

RATE CONSTANTS, ENERGIES AND ENTROPIES OF ACTIVATION FOR THE HYDROLYSIS OF METHYL ACETATE AND ETHYL *n*-BUTYRATE IN 70% ACETONE

	Methyl acetate		Ethyl *n*-butyrate	
	Exchange resin	HCl	Exchange resin	HCl
$10^5k_{12.5}$	0.881	1.59	0.0866	0.577
	0.881	1.57	0.0863	0.586
10^5k_{25}	2.70	5.45	0.255	1.92
	2.74	5.44	0.256	1.91
$10^5k_{37.5}$	8.15	17.3	0.722	5.96
	8.18	17.5	0.718	5.93
$E_{25-12.5}{}^a$	15,300	16,800	14,700	16,100
$E_{37.5-25}$	16,200	17,100	15,200	16,700
$\Delta\Delta S^{\ddagger b}{}_{25-12.5}$	−6.5		−9.0	
$\Delta\Delta S^{\ddagger}{}_{37.5-25}$	−4.5		−8.9	

^{a} Calories. ^{b} $S\,\Delta\Delta^{\ddagger} = \Delta S^{\ddagger}_{\text{Resin}} - \Delta S^{\ddagger}_{\text{HCl}}$ (cal./deg.).

An Absorption Experiment.—When the air-dry exchange resin was mixed with 70% acetone there was 40% increase in the apparent volume of the resin. It was of interest to determine if there was selective absorption of the components of solutions of fatty acids in 70% acetone.

Solutions of caproic acid and of acetic acid in 70% acetone were prepared; these were mixed with the exchange resin in the proportion of 25 ml. of solution to 10 g. of air-dry resin. After agitation and settling of the solid, 1-ml. samples of the supernatant liquid were removed, added to 50 ml. of distilled water, and titrated with standard alkali in the presence of phenolphthalein. Blanks of 1 ml. from 70% acetone in contact with resin required 0.10 ml. of 0.05185 *N* alkali for neutralization just after mixing and 0.14 ml. after ten days in contact with the resin. Table VI shows the results.

TABLE VI

CONCENTRATION OF ACID BEFORE (C_{Acid}) AND AFTER (C'_{Acid}) ABSORPTION OF AQUEOUS ACETONE SOLUTIONS OF CARBOXYLIC ACIDS BY AN EXCHANGE RESIN

"Concentration" of resin: 0.40 g. per ml. of solution

Acid solution	C_{Acid}	C'_{Acid}	Increase, %
Caproic acid	0.312	0.383	22.8
Acetic acid	.353	.410	16.2

These results show that the solvent is absorbed in preference to the acid in the case of caproic acid and acetic acid, and that acetic acid is absorbed to a greater degree than caproic acid.

Errors

At 25° the average deviation of the mean of the k values is ±0.2% for hydrogen chloride-catalyzed experiments and ±0.5% for resin-catalyzed experiments. Residual errors in temperature, concentration of ester, concentration of hydrochloric acid and other factors are expected to increase the precision measure in the k values to ±1% for both hydrogen chloride and resin-catalyzed reactions.

The precision measure for energies of activation is ±200 calories per gram mole, and the precision measure for relative entropies of activation is ±1 calorie per degree.

Discussion

Whatever the detailed mechanism of the catalysis of hydrolysis by strong aqueous acids, there is every reason to suppose it to be the same for the resin, a strong acid of essentially infinite molecular weight, as for the homogeneous acid. It involves therefore for both a positively charged transition state in which a proton has been transferred to the ester molecule from the oxonium ion of the acid. If, as the present results indicate, diffusion rates are fast enough so that the chemical process is rate determining, the difference in rate between heterogeneous and homogeneous cases depends upon the fact that, in the former, both the oxonium ion and the charged transition state are restricted by electostatic forces to the immediate neighborhood of the negatively charged RSO_3^- groups in the resin. More specifically the ratio $k_{\text{resin}}/k_{\text{HCl}}$ is determined by the difference

$$F^{\ddagger}_{\text{resin}} - F^{\ddagger}_{\text{HCl}} - F^{\circ}_{\text{resin}} + F^{\circ}_{\text{HCl}}$$

in which the $F^{\ddagger}$'s are the standard free energies of the transition states for the resin and hydrogen chloride cases and the F°'s are the standard free energies of oxonium ion in the resin system and in the hydrochloric acid solution, respectively.

This quantity is observed to be positive in the cases studied and increases rapidly and nearly linearly (Fig. 2) with increasing chain length of the ester molecule. The positive free energy difference results from negative values of the corresponding heat content and entropy differences, the latter being therefore predominant in effect. The heat content difference of about −1.3 kcal. is little if any affected by chain length, the entropy difference changes from −5.5 cal./deg. with methyl acetate to −9.0 with ethyl *n*-butyrate. It appears therefore that the major factor in the effects observed is the loss in internal entropy of the ester molecule accompanying its fixation on the skeleton of the resin catalyst in the formation of the transition state. This conclusion is consistent with the fact that the longer chain ester, having more internal entropy, loses more in the formation of the transition state. Translational entropies, on the other hand, and all effects which depend on the electrical charge of the transition state should to a first approximation cancel out between the transition state and the oxonium ion.

This interpretation of the kinetic results is related to the one given by Barrer[7] for the equilibrium in the absorption of hydrocarbons by zeolites. It is supported by the results reported in Table VI which show that the longer chain molecule caproic acid is less strongly absorbed by the ion exchange resin than the shorter chain molecule acetic acid.

Effects of this sort may very well be important in the general problem of heterogeneous catalysis and in that of enzyme action, although there is no exact correspondence, either qualitative or quantitative, between the net effect observed in these cases and those reported here for the exchange resin catalysis. Thus the energy of activation for the catalysis by yeast saccharase of the inversion of saccharose near the optimum *p*H is 17 kcal. less than for the hydrochloric acid catalyzed reaction,[8] and low temperature coefficients have also been observed[9,10] for other enzyme catalyzed reactions. Further the efficiency of pancreatic lipase in the hydrolysis of esters in water increases with chain length from ethyl acetate to ethyl *n*-butyrate.[10]

It appears however that the balance of conflicting effects may lead to considerable difference in the behavior of the catalysis by an ion exchange resin according to the particular resin used and the medium. Thus Thomas and Davies[11] have reported that the resin Amberlite IR-100 is more efficient than hydrochloric acid for the hydrolysis of aliphatic esters in water and that its efficiency increases with increasing chain length. And Levesque and Craig[12] using Amberlite IR-100 for the

[7] Barrer and Ibbitson, *Trans. Faraday Soc.*, **40**, 195 (1944); Barrer, *ibid.*, p. 374; *Ann. Rep. Chem. Soc.*, **41**, 31 (1944).

[8] Nelson and Bloomfield, THIS JOURNAL, **46**, 1025 (1924).

[9] Sumner and Somers, "Chemistry and Methods of Enzymes," Academic Press, New York, N. Y., 1947, p. 18.

[10] Kastle and Loevenhart, *Am. Chem. J.*, **24**, 491 (1900).

[11] Thomas and Davies, *Nature*, **159**, 372 (1947).

[12] Levesque and Craig, *Ind. Eng. Chem.*, **40**, 96 (1948).

esterification of oleic acid with *n*-butanol obtained specific rates very nearly proportional to the external area of the resin particle employed, indicating that only acid groups near the exterior of the particles are active catalytically. The present results on the effect of particle size of resin, obtained with much smaller molecules, also indicate a superiority of the external acid groups, but one which is of almost negligible total effect. One might attribute this effect to the intrusion of diffusion into the interior of the particle as a significant factor in the control of the over-all rate except that the effect of particle size is unchanged by a change in the size of the reacting molecule which produces a large change in the over-all rate.

Summary

A method in which reproducible rate constants can be obtained has been developed for following the hydrolysis of esters in 70% acetone with a cation exchange resin as the catalyst. A comparison of the catalytic effect of the exchange resin with that of hydrochloric acid showed that the free energy of activation relative to the hydrogen chloride-catalyzed reaction increased almost linearly with the chain length of the ester in the series methyl acetate, ethyl acetate, ethyl *n*-butyrate, ethyl *n*-caproate at 25°.

Measurements of the temperature coefficients of the rates of hydrolysis of methyl acetate and of ethyl *n*-butyrate showed that the lower rates with the exchange resin were accompanied by lower entropies of activation and lower heats of activation than with hydrochloric acid, the former effect being strongly dependent on the chain length of the ester, the latter relatively independent.

The major factor determining these effects appears to be the loss in internal entropy of the ester molecule which accompanies its fixation on the skeleton of the resin catalyst in the formation of the transition state.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF ILLINOIS INSTITUTE OF TECHNOLOGY AND RCA LABORATORIES]

Absorption Spectra of Some Double Salts Containing Bivalent Cobalt[1]

BY MELVIN L. SCHULTZ[2]

The absorption spectra of crystals of five double salts of cobaltous chloride all containing the tetrahedral CoCl$_4^{--}$ ion have been shown[3] to consist, at room temperature, of a large number of relatively narrow bands. The details of these spectra were found to be almost completely independent of the identity of the cation and therefore it was concluded that the absorption was characteristic of the complex ion.

Prominent among the wave number differences of adjacent bands in these spectra is one of approximately 370 cm.$^{-1}$. This frequency was identified tentatively as one of the characteristic frequencies of the CoCl$_4^{--}$ ion. The validity of this interpretation has, in the present work, been investigated by studying the spectra of two salts, (PyH)$_2$CoBr$_4$ and (QuH)$_2$CoBr$_4$,[4] containing the corresponding bromo- complex ion. Substitution of one halogen for another would be expected to lead to changes in frequency differences if the structure of the spectrum is determined by the coupling of vibrations of the complex with electronic transitions.

Such an effect has, in fact, been observed by Brode and Morton[5] for solutions of cobaltous halides in concentrated aqueous solutions of the corresponding hydrogen halides.[6] They found decreasing separations of bands in passing from the chloride to the bromide and to the iodide. Their analysis is subject to some uncertainty, however, since the absorption bands of the solutions are broad and incompletely resolved. The comparison in the case of the crystals is much more clear cut since the bands are considerably sharper and therefore more completely resolved. The expected frequency shifts have been found for many, but not all, of the bands in the spectra of the crystals.

Confirmation of the hypothesis that the detailed structure of the spectra of these complexes of bivalent cobalt is determined essentially by the configuration of the complex ion was obtained by studying the absorption spectrum of crystals of 2(en H$_2$)Cl$_2$·CoCl$_2$.[7] Although the structure of the complex ion in this compound has not been determined, the coördination number of cobalt is probably six[8] with probably an octahedral arrangement of chloride ions about the central co-

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[1] The spectra described here were photographed in 1943 while the author was a member of the staff of Illinois Institute of Technology. The plates obtained were measured and the present paper was written after the author became associated with RCA Laboratories.

[2] Present address: RCA Laboratories Division, Radio Corporation of America, Princeton, N. J.

[3] M. L. Schultz and E. F. Lilek, THIS JOURNAL, **64**, 2748 (1942).

[4] The abbreviations Py, Qu and en represent pyridine, quinoline and ethylenediamine, respectively.

[5] W. R. Brode, *Proc. Roy. Soc.* (*London*), **118A**, 286 (1928); W. R. Brode and R. A. Morton, *ibid.*, **120A**, 21 (1928).

[6] These solutions also contain the CoX$_4^{--}$ ion; see reference 3.

[7] Due to lack of time, this spectrum was only incompletely investigated. Structure in the region of very strong absorption in the red was not resolved since sufficiently thin absorbing layers were not used.

[8] J. Meyer and K. Hoehne, *Z. anorg. allgem. Chem.*, **222**, 161 (1935).