

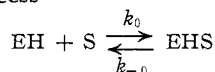
tially reactive enzyme-substrate complex, there is no other configuration of enzyme-substrate complex of greater stability. Strong arguments in favor of the former hypothesis are given below and elsewhere.⁶ In any case, the possibility of a "strained" enzyme-substrate complex, or any other catalytic mechanisms such that an energetically less favorable complex leads to a more favorable decomposition rate, is excluded.

Preliminary evidence from this Laboratory has indicated that the same arguments apply for the systems α -chymotrypsin-acetyl-L-phenylalaninamide.

It has recently been brought to our attention by Dr. M. Morales⁷ that K_M and K'_M for trypsin-benzoyl-L-arginine derivatives (ester and amide) must both be equilibrium constants (equal to k_2/k_1 and k'_2/k'_1 , respectively). This conclusion follows from observations of the pH dependence of the hydrolysis rate (v).⁸ The data correlate quantitatively with the equation

$$\frac{k_2[E_0]}{v} = \left(1 + \frac{K_M}{[S_0]}\right) \left(1 + \frac{[H^+]}{K_{EH}}\right) \quad (3.1)$$

where K_{EH} is assumed to be the dissociation constant of EH. Morales⁹ has shown that a necessary and sufficient condition for the above equation to hold is that $k_0/k_{-0} = k_2/k_1 = K_M$, where k_0 and k_{-0} refer to the process



(6) H. Gutfreund, *Discs. Faraday Soc.*, "Symposium on Rapid Reaction Kinetics," in press.

(7) M. Morales, private communication.

(8) H. Gutfreund, *THIS JOURNAL*, in press.

(9) M. Morales, not yet published. See as well, J. Botts and M. Morales, *Trans. Faraday Soc.*, **49**, 1 (1953).

It is of interest to note the consistency in the conclusions of Morales and this paper. On the basis of apparently different criteria, the hypothesis K_M is equal to k_2/k_1 seems evident.

The above equation 3.1 appears to be valid for the system acetylcholinesterase-acetylcholine as well,¹⁰⁻¹² indicating that the equilibrium assumptions of the previous paper are valid.

The evidence suggests that a detailed study of the forces of interaction between the proteolytic enzymes and amino acid derivatives (as in Paper I of this series) might be fruitful. It is of interest to note that the differences in K_M among acetyl-L-phenylalaninamide, acetyl-L-tyrosinamide and acetyl-L-tryptophanamide or among the corresponding nicotinyl derivatives¹³ can be correlated with the dispersion energy differences calculated by the method of the previous paper.

Acknowledgments.—The author is indebted to Dr. Herbert Gutfreund for many enlightening discussions, and detailed assistance with enzymatic preparations, and to Professor F. J. W. Roughton for making available the facilities of the Department of Colloid Science, Cambridge.

This work was done wholly under a fellowship from the American Cancer Society upon recommendation of the Committee on Growth of the National Research Council.

(10) I. B. Wilson and F. Bergmann, *J. Biol. Chem.*, **186**, 683 (1950).

(11) K. J. Laidler, *Trans. Faraday Soc.*, in press (1954).

(12) M. Dixon, *Biochem. J.*, **55**, 161 (1953).

(13) H. T. Huang, R. J. Foster and C. Niemann, *THIS JOURNAL*, **74**, 105 (1952).

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Magnetic Catalysis of Decarboxylation and Other Reactions¹

BY EDWARD GELLES AND KENNETH S. PITZER

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The effect of rare earth ions on the rate of decarboxylation of phenylmalonic acid in aqueous solution is reported. It is found that at 0.5 *M*, the highly paramagnetic dysprosium ion accelerates the rate by about 10% as compared to the results for the diamagnetic ions of lanthanum, yttrium and lutetium. Exploratory measurements indicate no magnetic catalysis for the non-enzymatic hydrolysis of urea but a possibly positive effect for the isomerization of maleic acid. Additional comments are included with respect to isotope effects on the rate of the decarboxylation reaction.

Recently we reported² preliminary results indicating a positive catalytic effect of dysprosium ion on the decarboxylation of phenylmalonic acid in aqueous solution. We are now presenting our final results on this reaction together with exploratory work on two other reactions.

Our interest was aroused in this subject by the peculiar results which had been reported on the effects of C¹³ and C¹⁴ on the rate of decarboxylation of malonic and related acids. This work has been

the subject of several recent reviews.³ The decrease in the rate on substitution of C¹⁴ for C¹² in the carboxyl group is reported in most cases to be substantially greater than twice the decrease on C¹³ substitution. Such results cannot be explained as effects of change of mass alone. Since C¹³ has a nuclear spin and magnetic moment, while both C¹² and C¹⁴ have zero values for these quantities, it seemed desirable to investigate the possible effects of the inhomogeneous magnetic field that such a magnetic moment would cause. Certain rare earth ions have

(1) This research was assisted by the American Petroleum Institute through Research Project 50. The dysprosium and lutetium were kindly made available to us by Dr. F. H. Spedding.

(2) K. S. Pitzer and E. Gelles, *THIS JOURNAL*, **75**, 5132 (1953).

(3) (a) P. E. Yankwich, *Ann. Rev. Nuclear Sci.*, **3**, 235 (1953); (b) H. G. Thode, *Ann. Rev. Phys. Chem.*, **4**, 95 (1953); (c) J. Bigeleisen, *J. Phys. Chem.*, **56**, 823 (1952).

very large magnetic moments while others have zero magnetic moment. Hence this system was selected for the investigation of magnetic moment effects.

Magnetic Catalysis of Chemical Reactions.—The effect of magnetic fields on the rates of chemical reactions has been the subject of considerable discussion.⁴ There is little definite experimental evidence that external magnetic fields exert significant influence on the rates of any chemical reactions at ordinary temperatures. Catalysis of some homogeneous chemical reactions by paramagnetic substances has been reported, but the available evidence is not very conclusive. An example of particular relevance is the catalysis of *cis-trans* isomerization reactions by paramagnetic gases and ions in solution.⁵

A study of the kinetics of a number of *cis-trans* isomerization reactions shows that some of these reactions have an abnormally low probability factor around 10^3 and an activation energy about 20 kcal. lower than that of isomerization reactions with a normal probability factor. Arguments have been presented that, if an excited electronic state for the ethylenic compound lies about 20 kcal. lower in energy than the transition state for the adiabatic isomerization from singlet to singlet state, then the abnormally low probability factors in some of these reactions can be accounted for semi-quantitatively on the basis of a non-adiabatic reaction by way of transition from singlet to the excited triplet electronic state.⁶ Eyring and Harman⁷ suggested that paramagnetic substances would increase the probability of transition from singlet to triplet state by providing a non-homogeneous magnetic field which will act differently on the two magnetic dipoles arising from the spin of the two electrons in the π -bond. An alternative explanation of catalytic action has been put forward by McConnell.⁸ He suggests that the catalyst in an electronic state other than singlet interacts with the singlet and triplet states of the isomer and that the resulting electronic states are such as to allow an alternative non-adiabatic reaction path.

As indicated above, we decided to study the effect of paramagnetic rare earth ions on the rate of a decarboxylation reaction and also, by way of comparison, on the rate of the non-enzymatic acid hydrolysis of urea where a normal $C^{14}:C^{13}$ isotope effect ratio slightly less than 2 has been found.⁹ Some experiments were also carried out on the *cis-trans* isomerization of maleic acid.

The effect of paramagnetic ions on reaction rates was compared in these studies with diamagnetic ions of the same charge and similar size. Experiments were carried out with La^{3+} , Y^{3+} , Lu^{3+} and Dy^{3+} ions at concentrations above 1 *N*. Dysprosium was chosen for its very high magnetic moment.

The basic assumption is made that the ordinary chemical effect of these added ions on the rate of a reaction, such as a salt or coordination effect, will

(4) P. W. Selwood, *Chem. Revs.*, **38**, 41 (1946).

(5) B. Tamamushi and H. Akijama, *Bull. Chem. Soc., Japan*, **12**, 382 (1937).

(6) J. L. Magee, W. Shand and H. Eyring, *THIS JOURNAL*, **63**, 677 (1941).

(7) R. H. Harman and H. Eyring, *J. Chem. Phys.*, **10**, 557 (1942).

(8) H. McConnell, *ibid.*, **20**, 1043 (1952).

(9) J. A. Schmitt and F. Daniels, *THIS JOURNAL*, **75**, 3564 (1953).

be a smooth function of ionic radius. The crystal radii of the rare earth ions decrease from La^{3+} to Lu^{3+} , and if that of La^{3+} is taken as 1 the radii of Dy^{3+} , Y^{3+} and Lu^{3+} are 0.84, 0.83 and 0.79. A review of the chemical behavior of rare earth ions under various chemical conditions shows that there is a close proportionality of activity and ionic radius in most cases.¹⁰⁻¹²

In many cases the activities of Y^{3+} and Dy^{3+} are nearly identical but there are some instances where the behavior of the former ion is slightly displaced toward La^{3+} . Experiments carried out with Lu^{3+} show however that in the decarboxylation reaction the diamagnetic Y^{3+} ion is an adequate basis for the evaluation of any effects associated with the paramagnetic character of Dy^{3+} .

Decarboxylation of Phenylmalonic Acid.—Preliminary experiments on the decarboxylation of phenylmalonic acid in aqueous solution at 45° have been reported by us previously.^{2,13}

Through an error the concentration of rare earth ion used in these early experiments was quoted as 0.5 *N* instead of the correct value of 0.5 *M*. Further experiments employing the same experimental technique are reported here.

The phenylmalonic acid was prepared as described previously.¹³ Most experiments were carried out in an oil thermostat at $45 \pm 0.02^\circ$. Rare earth solutions were prepared by solution of the oxides, obtained where necessary by ignition of the oxalates, in concentrated hydrochloric acid. Most of the hydrochloric acid was evaporated and the rare earth chlorides were taken up in water. Reaction mixtures were prepared from fresh phenylmalonic acid solutions and rare earth chloride solutions. The initial *pH* of the reaction mixtures was equalized by addition of standard hydrochloric acid. About 10 aliquots were withdrawn at various stages during each reaction, the rare earths were precipitated as oxalates, and the organic and mineral acids were estimated by titration with standard alkali using a Beckman *pH* meter. The rate coefficients thus obtained were in good agreement with earlier values derived from titrations with standard alkali using phenolphthalein indicator after expulsion of CO_2 . The present experiments were carried out in the approximate *pH* range 0.5–1.0 in which range decarboxylation is almost entirely due to the un-ionized dibasic acid.¹³ Even in this range however the first order rate coefficients are somewhat sensitive to *pH*. Table I gives some typical apparent first-order rate coefficients in hour⁻¹ units for the decarboxylation of phenylmalonic acid at 45° in the relevant *pH* range. In this and subsequent tables the rate coefficients are obtained from a first-order logarithmic plot for the first 35–50% of the reaction



and are considered accurate to ± 3 to 4%.

In this *pH* range decarboxylation is due to the undissociated phenylmalonic acid only, and the drift of rate coefficients with *pH* is to be attributed

(10) T. Moeller and H. E. Kremers, *Chem. Revs.*, **37**, 97 (1945).

(11) B. H. Ketelle and G. E. Boyd, *THIS JOURNAL*, **69**, 2800 (1947).

(12) E. J. Wheelwright, F. H. Spedding and G. Schwarzenbach, *ibid.*, **75**, 4196 (1953).

(13) E. Gelles, *ibid.*, **75**, 6199 (1953).

TABLE I

| Phenylmalonic acid, <i>M</i> | 0.068 | 0.054 | 0.057 | 0.050 | 0.062 | 0.067 | 0.054 |
|------------------------------|-------|-------|-------|-------|-------|-------|-------|
| Added HCl, <i>N</i> | .213 | .200 | .166 | .138 | .132 | .124 | .120 |
| $10^3 k$ | 10.0 | 10.0 | 10.4 | 10.5 | 10.6 | 10.8 | 10.8 |

to activity effects. The limiting rate constant for the undissociated dibasic acid calculated¹⁸ from experiments at higher *pH* is 11.2×10^{-3} hour⁻¹. The above rate coefficients are not therefore strictly comparable with those in the presence of rare earths unless experiments are carried out at constant ionic strength and *pH*.

Comparison of the effects of different rare earths can be made by adjusting the initial *pH* by addition of standard acid. A typical experiment in which such a comparison is made is shown in Table II.

TABLE II

pH 0.75 ± 0.03 throughout; rare earth 0.48 *M*; phenylmalonic acid 0.070 *M*.

| | Blank | La ³⁺ | Y ³⁺ | Dy ³⁺ | Lu ³⁺ |
|---------------------|-------|------------------|-----------------|------------------|------------------|
| Added HCl, <i>N</i> | 0.213 | 0.136 | 0.130 | 0.121 | 0.110 |
| $10^3 k$ | 10.0 | 10.1 | 10.1 | 12.0 | 10.7 |

The amount of added HCl listed gives an indication of the trend in the degree of hydrolysis of the rare earths in the reaction mixtures, but is not of quantitative significance as the initial *pH* of these reaction mixtures differed slightly within the range given above. Although the rate coefficient for the blank experiment is not strictly comparable with those in the presence of rare earths, it may be seen that the diamagnetic rare earth ions have little effect on the rate of decarboxylation, but that the paramagnetic Dy³⁺ ion leads to a definite acceleration in rate.

A summary of some other experiments is given in Table III.

The added HCl concentration listed is the mean concentration for the different rare earth salts in each set of experiments adjusted to the same initial *pH*. These typical experiments at different *pH* and rare earth concentrations show, as did the data in Table II, that the decarboxylation reaction is cata-

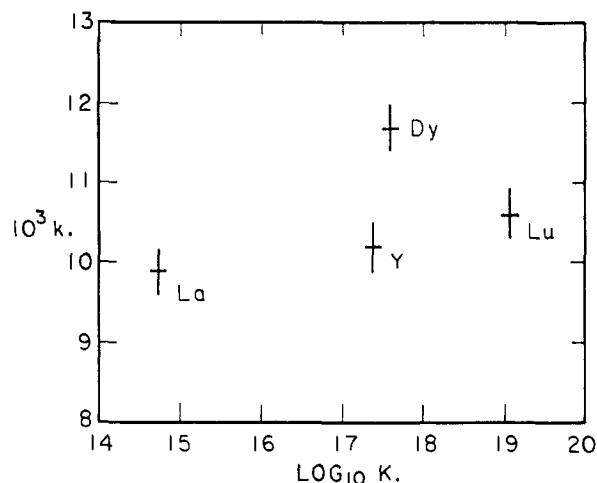


Fig. 1.—The rate constants for the decarboxylation of phenylmalonic acid in the presence of the indicated rare earth ions. The abscissa are equilibrium constants for rare earth ion complex formation—see text.

TABLE III

DECARBOXYLATION OF PHENYLMALONIC ACID AT 45°

| Rare earth, <i>M</i> | 0.38 | 0.48 | 0.48 | 0.48 | 0.48 | 0.92 |
|------------------------------|------|------|------|------|------|------|
| Phenylmalonic acid, <i>M</i> | .067 | .046 | .070 | .049 | .057 | .062 |
| Added HCl, <i>N</i> | .120 | .120 | .125 | .138 | .166 | .122 |
| $10^3 k$ (La ³⁺) | | | 10.1 | 9.8 | | |
| $10^3 k$ (Y ³⁺) | | 10.2 | 10.1 | 10.3 | 10.3 | 10.6 |
| $10^3 k$ (Dy ³⁺) | 11.4 | 11.5 | 12.0 | 11.8 | 11.6 | 12.2 |
| $10^3 k$ (Lu ³⁺) | 10.5 | | 10.7 | | | |

lyzed by the Dy³⁺ ion, the diamagnetic rare earth ions La³⁺, Y³⁺ and Lu³⁺ having little effect on the reaction.

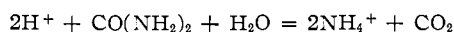
For purposes of comparison at a rare earth concentration of 0.48 *M* and at the mean *pH* for the experiments in Table III we may take rate coefficients of $10^3 k = 9.9, 10.2, 11.7$ and 10.6 for La³⁺, Y³⁺, Dy³⁺ and Lu³⁺ ions, respectively. The relative accuracy of these coefficients should be within ±3%. Figure 1 shows a plot of these rate coefficients against the logarithm of the equilibrium constants for the reaction of these ions with ethylenediaminetetraacetic acid.¹² Any other quantity depending directly on the chemical activity of the rare earth ion or indeed the crystal radii will result in a similar plot with slight displacements in the abscissa.

It is apparent that the acceleration of this decarboxylation reaction by Dy³⁺ is connected with the unpaired electrons of the latter ion. Without going further into the possible mechanism of this magnetic catalysis at this point it is clear that the presence of the paramagnetic dysprosium ion near the reacting molecule leads to a change in the chemical bonding in the transition state of reaction specifically by nature of the unpaired 4*f* electrons in the rare earth ion. The present experiments are not sufficiently accurate in view of the size of the observed effects to allow a study of the degree of magnetic catalysis with the magnetic moments of different paramagnetic ions or with the concentration of such ions. Preliminary experiments with Gd³⁺ and Dy³⁺ below 0.1 *M* yielded effects which were within experimental error. No further work was done with gadolinium. At higher concentrations the acceleration in the presence of Dy³⁺ ions seems to approach saturation, which is understandable if short range electrostatic interactions have led to the proximity of a rare earth ion to each phenylmalonic acid molecule.

Acid Hydrolysis of Urea.—The acid hydrolysis of urea was studied in the following manner. Solutions containing weighed amounts of urea (Reagent grade, recryst. from alcohol, m.p. 132°) were made up at room temperature to a given volume with standard rare earth chloride solutions containing excess hydrochloric acid. The solutions were prepared from weighed amounts of the pure ignited oxides and the final concentration of acid was equalized with standard hydrochloric acid. Sealed tubes containing 4-cc. samples of the reaction mixtures were heated in an oil thermostat at $100.0 \pm 0.2^\circ$. Tubes were removed at various times and quenched. The contents were washed into beakers, the rare earths precipitated with 5 cc. of saturated potassium oxalate solution, and the extent of hydrolysis determined by titration of the excess acid with standard sodium hydroxide using

a Beckman pH meter. The rate of hydrolysis found in the absence of rare earths was in excellent agreement with previous measurements.¹⁴

The apparent first-order rate coefficients, in min.⁻¹ units, were calculated for the reaction



on the basis of the total urea concentration. These coefficients are constant throughout the entire course of a given reaction.

TABLE IV
ACID HYDROLYSIS OF UREA AT 100°

Initial urea 0.05 *M*; initial pH 0.90; added HCl 0.096*N*; rare earth ion 0.46 *M*.

| | Blank | La ³⁺ | Y ³⁺ | Dy ³⁺ |
|--------------|-------|------------------|-----------------|------------------|
| 10% <i>k</i> | 1.01 | 0.72 | 0.63 | 0.56 |

It is clear that the paramagnetic Dy³⁺ ion does not increase the rate of the reaction; indeed there appears to be a depressing effect in relation to the rate in the other solutions. We do not believe any definite conclusion is justified, however, because of the limited accuracy of the single exploratory experiment and because of the substantial shifts in rate between the blank, the La³⁺, and the Y³⁺ solutions.

Isomerization of Maleic Acid.—The *cis-trans* isomerization of maleic acid was followed by determining the rate of formation of the sparingly soluble fumaric acid.¹⁵ Reaction mixtures of known amounts of maleic acid, rare earth chloride and hydrochloric acid were prepared in a manner similar to the urea experiments. Reagent grade maleic acid was recrystallized from water, m.p. 130°. The initial acid concentration was equalized in each set of experiments. 4-Cc. samples in sealed tubes were heated for various times at 100 ± 0.2°. After removal from the oil thermostat the tubes were placed in an ice-bath for 8 hours. The precipitated fumaric acid was filtered off on a sintered glass filter, washed with 1 cc. of ice-cold water, dried and dissolved in a known amount of standard sodium hydroxide. The excess alkali was determined by titration with standard hydrochloric acid using phenolphthalein as indicator. The con-

TABLE V

cis-trans ISOMERIZATION OF MALEIC ACID AT 100°

Initial maleic acid 0.48 *M*; added HCl 1.06 *N*; rare earth ion 0.37 *M*; fumaric acid from 4 cc. reaction mixture (equiv. vol. cc. 0.1 *N* NaOH).

| Time, hr. | Blank | La ³⁺ | Y ³⁺ | Dy ³⁺ |
|-----------|-------|------------------|-----------------|------------------|
| 9.67 | 5.3 | 12.6 | 13.4 | |
| 14.0 | 8.8 | 16.6 | 17.7 | 18.5 |
| 21.0 | 11.8 | 20.0 | 20.3 | 21.0 |

| Initial maleic acid 0.50 <i>M</i> ; added HCl 1.13 <i>N</i> ; rare earth ion 0.38 <i>M</i> | | | | |
|--|--|--|------|------|
| 3.0 | | | 6.4 | 6.7 |
| 6.0 | | | 12.4 | 13.2 |
| 9.0 | | | 15.3 | 16.0 |
| 12.0 | | | 18.4 | 19.3 |

(14) C. E. Fawsitt, *Z. physik. Chem.*, **41**, 601 (1902); E. A. Werner, *J. Chem. Soc.*, **113**, 84 (1918).

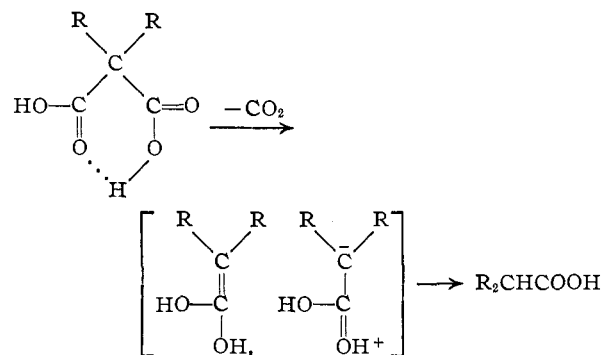
(15) K. Nozaki and R. Ogg, *THIS JOURNAL*, **63**, 2583 (1941). See also D. H. Derbyshire and W. A. Waters, *Trans. Faraday Soc.*, **45**, 749 (1949); H. Taube, *THIS JOURNAL*, **65**, 526 (1943).

centration of maleic acid used in these experiments was 0.50 *M*. The solubility of fumaric acid in water at 0° is 0.035 *M*. The solubility of fumaric acid is assumed to be the same in the presence of equal concentrations of different rare earths. Owing to the number of side reactions accompanying the *cis-trans* isomerization of maleic acid in HCl solutions,¹⁵ no rate constants were calculated from the data for this reaction. The results are simply expressed as the volumes of 0.1 *N* alkali equivalent to the amounts of fumaric acid formed (uncorrected for solubility at 0°) at different stages of reaction.

The results suggest an increased rate in the presence of the Dy³⁺ ion that may be ascribed to its paramagnetic character. But this conclusion depends on the validity of taking Y³⁺ as a basis for the comparison with a diamagnetic ion of almost identical chemical activity, and this is by no means certain. Also the magnitude of the effect is dangerously close to the possible experimental error. We regard our results as inconclusive but note that there are other indications of magnetic catalysis of this reaction.⁵

Discussion.—While we believe our results definitely establish a positive catalytic effect of Dy³⁺ in the decarboxylation of phenylmalonic acid, the effect is so small that its further investigation is not easy. Also it is not clear whether the corresponding effect of the nuclear magnetic moment of C¹³ would be appreciable or not.

A possible detailed mechanism involves the activated complex formulation given first in the preceding paper¹³



If the normal geometry of a malonic acid is examined, one finds that the two R groups are in a plane perpendicular to the C-C-C skeleton of the acid. Thus in the activated complex the C-C double bond is twisted out of the plane by 90°, *i.e.*, it is in the activated complex state for *cis-trans* isomerization. Arguments have been presented previously in favor of a triplet electronic state for this atomic configuration. Our results would be explained if the presence of the dysprosium ion allowed about 10% additional reaction through a triplet activated complex in addition to the normal rate through a singlet activated complex.

Finally, we wish to make certain comments on the isotope effects and upon interpretations of a calculation published previously by one of us.¹⁶ This calculation applies to either the intramolecular or the intermolecular isotope effect of a malonic acid

(16) K. S. Pitzer, *J. Chem. Phys.*, **17**, 1341 (1949).

with C¹⁴ substitution in the carboxyl group.¹⁷ All parameters were adjusted to maximize the result within the limits of reasonable force constants and other molecular parameters. The resulting 14% effect exceeds all well established observations, consequently there is no reason to question statistical rate theory. There is no difficulty in the selection of other reasonable parameters which yield smaller isotope effects.

The basic formula used by various workers is

$$\frac{k}{k'} = \left(\frac{\mu'}{\mu}\right)^{1/2} \left[1 + \sum_{i=1}^{3N-6} G(u_i) \Delta u_i - \sum_{j=1}^{3N-7} G(u_j^{\ddagger}) \Delta u_j^{\ddagger} \right]$$

where k is a rate constant, μ a reduced mass for the reaction coordinate, the primes indicate the isotopically substituted species, and the G 's and u 's are the functions defined by Bigeleisen and Mayer.¹⁸ In the earlier calculation of one of us,¹⁶ it was as-

(17) An erroneous statement that this calculation is not applicable to the intramolecular isotope effect is made by Bigeleisen in ref. 3c.

(18) J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.*, **15**, 261 (1947).

sumed that substitution of C¹⁴ (or C¹³) in the carboxyl group which is *not* undergoing reaction would have no effect on the rate. In the formula this arises because, for any vibration in the non-reacting portion of the molecule, there are corresponding $G(u)\Delta u$ terms in the first sum for the initial molecule and in the second sum for the activated complex. If the binding of the non-reacting portion of the molecule is unchanged in the activated complex, then these terms are equal and cancel. Actually, it is quite possible that the binding in these non-reacting portions of the molecule may change. Certain calculations¹⁹ have been published, however, in which mathematical approximations yield spurious effects for isotopic substitution in the non-reacting carboxyl group.

(19) Bigeleisen (references cited in 3c) neglects the second sum of $G(u)\Delta u$ (for the activated complex) and thus fails to obtain the cancellation of terms for the stretching vibration of the bond which is not broken.

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[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

Residual Paramagnetism and the Susceptibility of Some Isoelectronic Cobaltamines

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RECEIVED NOVEMBER 5, 1954

The molar magnetic susceptibilities of $[\text{Co}(\text{NH}_3)_5\text{HCO}_2]\text{I}_2$ and $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{I}_2$ were determined by the Gouy method to be $(-72.0 \pm 4.6) \times 10^{-6}$ and $(-45.2 \pm 2.5) \times 10^{-6}$, respectively. "Residual paramagnetism" of Co(III) appears to be $+141 \times 10^{-6}$ and $+165 \times 10^{-6}$, respectively, in contradiction to the prediction of Rosenbohm of $+60 \times 10^{-6}$ for each. Observations of Proctor and Yu on the shift of the nuclear resonance frequency of cobalt in cobalt complexes lead us to suggest the existence of low lying excited electronic levels for these two complexes to account for the observed small diamagnetism.

In the interpretation of the magnetic moments of complex compounds, it is assumed that the several atoms contribute additively to the magnetic susceptibility independent of the nature of the complex. In his extensive investigation of cobalt(III)-ammine complex compounds, Rosenbohm² found that a constitutive correction had to be included for Co(III) if conventional diamagnetic increments were to be used for the other atoms. His corrections were $+55 \times 10^{-6}$ for hexammines, $+60 \times 10^{-6}$ for pentammines, and $+73 \times 10^{-6}$ for tetrammines. We question whether such a constant constitutive correction can have validity since it ignores the specific effect of coordinated groups on the electronic distribution in the entire complex. We have therefore measured the magnetic moments of two isoelectronic cobalt(III)-ammines; $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{I}_2$ and $[\text{Co}(\text{NH}_3)_5\text{HCO}_2]\text{I}_2$. Since the nitro group and the formate group are similar in structure and isoelectronic, they should contribute approximately equally to the diamagnetism. With the same constitutive correction applied to each complex because they are both pentammines, we are led to expect that the susceptibilities of these two compounds would differ only by the very small difference in the diamagnetism of a nitro group and a formate group.

(1) General Electric Company, Pittsfield, Massachusetts.
(2) E. Rosenbohm, *Z. Physik. Chem.*, **93**, 693 (1919).

Experimental

Preparation of Compounds.—Formatopentamminecobalt(III) iodide was made according to the method of Yatsimirski³ from chloropentamminecobalt(III) chloride, potassium formate and KI. Nitropentamminecobalt(III) iodide was made according to the method described by Walton⁴ for the preparation of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{++}$ from chloropentamminecobalt(III) chloride, followed by precipitation with a saturated solution of KI. During purification by repeated crystallization, all of the nitrito salt $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{I}_2$ was converted to the more stable nitro salt $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{I}_2$.

Cobalt content was determined by the Volhard method as described by Treadwell and Hall⁵ and modified by Streuli.⁶ The salts were ignited to oxide and slowly digested in concentrated H_2SO_4 . Slow digestion using a barely warm hot plate and infrared heating gave pink CoSO_4 after 10–12 hours. A final oven bake for one hour at 450–500° drove off all acid and water. The temperature of the final baking must be regulated carefully to prevent formation of oxide from the sulfate.

Iodine content was determined by the method described by Treadwell and Hall⁷ using excess nitrite salt, acid and urea.

Results of the analyses are compared in Table I with theoretical values. The experimental values given are on the basis of four analytical determinations in triplicate on the formate salt and three determinations in triplicate on the nitro salt.

(3) K. Yatsimirski, *Zhurnal Obshchei Khimii*, **20**, 1408 (1950).

(4) H. Walton, "Inorganic Preparations," Prentice-Hall, New York, N. Y., 1948, p. 92.

(5) F. Treadwell and W. Hall, "Analytical Chemistry," Vol. II, 9th Ed., John Wiley and Sons, New York, N. Y., 1942, p. 603.

(6) C. A. Streuli, Thesis, Cornell University, Ithaca, N. Y., 1950.

(7) Reference 5, Vol. II, 8th Ed., 1935, p. 134.