[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

A Study of the Interchange between Chromioxalate Ion and Oxalate Ion, Using Radio-carbon[1]

BY F. A. LONG

Studies by Rideal and Thomas[2] and by Beese and Johnson[3] have shown that optically active chromioxalate ion in aqueous solution undergoes a first order racemization which is comparatively rapid at room temperature. The speed of racemization is unaffected by addition of oxalate ion but shows a slight positive ion catalysis.[3] To explain this racemization Thomas[4] proposed a mechanism which involves an ionization of the chromioxalate ion as the rate determining step

$$d \text{ or } l \ [Cr(C_2O_4)_3]^{=} = [Cr(C_2O_4)_2]^{-} + C_2O_4^{-}$$
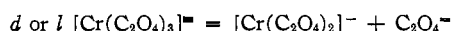
and subsequently a rapid recombination with concomitant loss in optical activity. Johnson,[3] because of the lack of influence of added oxalate ions on the rate of the reaction, states that the mechanism probably does not involve an ionization but is rather an intramolecular rearrangement.

The use of oxalate ion in which the carbon atoms are radioactive should permit an experimental test of the validity of the ionization mechanism. If some radioactive oxalate ions are present in solution with some chromioxalate ions and there is observed a transfer of radioactivity from the oxalate ions in solution to those in the coördination compound at a rate comparable with the rate of racemization, then the ionization mechanism would be indicated. If, on the other hand, there were no transfer of radioactivity this would suggest that the mechanism is some sort of intramolecular rearrangement.

This experiment has been tried and has resulted in no interchange, which makes the ionization mechanism seem very unlikely.

Preparation of Materials.—Radio-carbon, the C^{11} isotope, was prepared by bombarding fused boron oxide with high energy deuterons. The bombarding was done with the cyclotron of the Department of Physics, Cornell University, through the kind coöperation of Professor M. S. Livingston, Dr. M. Halloway and Mr. B. Moore. The deuteron source gave a current of around 10 microamperes at an energy of 1.1 MEV. The targets of boron oxide were activated, in general, for about thirty minutes.

The irradiated boron oxide containing the radio-carbon in the form of carbon dioxide and carbon monoxide[5] was placed in a platinum boat in a furnace which was maintained at about 800°. Ordinary carbon dioxide was passed over this melt and then over hot copper oxide to oxidize the carbon monoxide. About 200 ml. of carbon dioxide containing, in part, the radio-carbon was finally obtained.

The carbon dioxide was then converted into potassium oxalate by passing it into an evacuated flask which contained hot molten potassium mixed with coarse sand. After all the carbon dioxide had reacted the flask was cooled and the excess potassium was decomposed by careful addition of water. This solution was acidified to decompose the carbonate that was formed as a side reaction, treated with charcoal to decolorize it, filtered and brought to neutrality. In this way a solution of potassium oxalate was obtained in approximately 50% yield. The elapsed time, from the finish of the activation of the boron oxide target to the time when the potassium oxalate solution was obtained, averaged about twenty-five minutes.

Potassium chromioxalate was prepared by treating potassium dichromate with the proper amounts of potassium oxalate and oxalic acid according to the method of Croft.[6] The product was purified by recrystallization from an alcohol–water mixture and then from pure water. Analysis for chromium and oxalate content checked with the calculated. The final product in aqueous solution gave no precipitate with either silver or calcium ions, showing the absence of any uncombined oxalate ions.

Experimental Procedure.—Two methods were used to test for interchange between chromioxalate ion and oxalate ion. One was to place radioactive oxalate ion in solution with the chromioxalate ion and, after an interval of time, remove the oxalate ion and compare its radioactivity with that of the original oxalate. The other method was to precipitate the chromioxalate from the mixture and look for any radioactivity in it. The latter method is in general more satisfactory but was somewhat difficult in this case since most chromioxalate salts are rather soluble.

Some of the experimental details and reasons for them follow:

(1) The temperature at which the interchange was studied was 35.0 ± 0.2°. According to the data of Beese and Johnson[3] the half-time for the inversion reaction at 18.2° for an 0.08 M solution of d-chromioxalate ion is fifty-nine minutes. Using this value and the value for the heat of activation that is given by Rideal and Thomas,[2] 9.65 kcal., the half-time for the reaction at 35° is calculated to be twenty-four minutes. This is rapid enough to allow a clear test of the interchange to be made.

(2) The concentrations in the final solution were

(1) Presented at the Ninety-sixth Meeting of the American Chemical Society, Milwaukee, Wisconsin, September, 1938.

(2) Rideal and Thomas, J. Chem. Soc., 121, 196 (1922).

(3) Beese and Johnson, Trans. Faraday Soc., 31, 1632 (1935).

(4) Thomas, J. Chem. Soc., 119, 1140 (1921).

(5) Yost, Ridenour and Shinohara, J. Chem. Phys., 3, 133 (1935).

(6) Croft, Phil. Mag., 21, 197 (1842).

0.06 molar chromioxalate ion and approximately 0.012 molar oxalate ion. This latter value varied somewhat from run to run but never more than about 20%. When the determination of a possible interchange was made by following the change in radioactivity of the added, uncombined oxalate ions, these concentrations were such as to give a large percentage change if the interchange did parallel the inversion reaction.

(3) The radioactivity of the uncombined oxalate ion was followed by precipitating it as silver oxalate and then examining the radioactivity of the precipitate. Preliminary tests showed that it was possible to remove oxalate ions quantitatively from a solution containing chromioxalate ion without precipitating any of the latter substance. Further tests showed that it was possible to take a solution of radioactive potassium oxalate, remove several equal amounts of solution, precipitate out the oxalate ion from each as silver oxalate, and obtain values for the amount of radioactivity that were reproducible to 2 or 3%.

The amount of radioactivity for a given precipitate, present in a thin layer on a filter paper, was determined by covering the precipitate with thin aluminum foil and placing this face down on an ionization chamber. The current from the chamber was measured with a vacuum tube electrometer circuit similar to the Barth circuit discussed by Penick.[7] This type of instrument gave ample sensitivity even for the comparatively weakly-activated samples that were being used.

After preliminary tests had shown that the method was sufficiently accurate to detect any considerable interchange, two runs were made. The procedure was the same in each case. One hundred ml. of a solution containing about 0.025 molar radioactive oxalate ion was divided into two parts. Twenty-five ml. was added to 75 ml. of 0.033 molar silver nitrate solution. The silver oxalate was filtered off and the radioactivity of this control sample, Sample I, was determined. The remaining 75 ml. of potassium oxalate solution was mixed with 75 ml. of 0.12 molar potassium chromioxalate which previously had been heated in a thermostated water-bath to 35°. Fifty ml. of this mixture was withdrawn immediately, added to 50 ml. of 0.05 molar silver nitrate solution and filtered as before. The time of withdrawal of this sample, Sample II, was called zero time. At ensuing times of twelve and a half and twenty-five minutes two more 50-ml. samples, III and IV, were withdrawn, added to silver nitrate solution and filtered. The amount of silver oxalate that was obtained was, of course, identical for each of the samples. These four samples, one a control, one removed at the time of mixing, and one each at times of twelve and a half and twenty-five minutes, were then tested for their radioactivity over a period of one and one-half to two hours.

At least seven readings on the radioactivity of each sample were obtained. In order to make the best comparison of the various samples, the readings for the radioactivity for each sample were plotted as a function of time on semilogarithmic paper. The points fell closely on straight lines and for each sample the best straight line was drawn through the points. As an indication of the

accuracy of the readings, the values of the half-life of radio-carbon as calculated from the experimental curves varied from 20.2 to 20.9 minutes with an average of 20.5. The accepted value in the literature is 20.5 minutes.[8]

If, for a given run, one definite time is taken as zero time for plotting the radioactivity, then a comparison of the radioactivity of the various samples can be obtained by taking the values given by the straight lines at any single time. Table I gives such a comparison for the two runs that were made.

TABLE I

A COMPARISON OF THE RADIOACTIVITY OF SAMPLES OF SILVER OXALATE

The times for each sample are for the time at which the sample was withdrawn from the mixture of chromioxalate and oxalate ions. The figures give a comparison at a single time of the radioactivity for the samples for each run. The units are divisions of swing of the galvanometer.

Sample	I	II	III	IV
Time	Control	0	12.5	25
Run 1	5.72	5.79	5.47	5.02
Run 2	3.31	3.27	3.26	3.28

A third run was then made to look for any slight radioactivity in the chromioxalate ion. The procedure was very similar to the two preceding runs. The times at which samples were removed were slightly smaller, ten and twenty minutes. The chromioxalate was removed by mixing the filtrate from Sample IV, i. e., after the radioactive silver oxalate had been precipitated and removed, with excess hexamine cobaltinitrate. This precipitated the chromioxalate almost completely as $Co(NH_3)_6Cr(C_2O_4)_3$. This precipitate was washed and its radioactivity determined as before. Table II gives the results for this run. The original activation of the boron oxide was not as strong for this run as for the previous ones, but even so sufficient determinations of the radioactivity could be made on each sample to give a good half-life curve.

TABLE II

Samples I to IV are the same as in Table I except for the time intervals. Sample V is for the precipitated $Co(NH_3)_6Cr(C_2O_4)_3$ formed from the filtrate of Sample IV. The figures again give relative radioactivity.

Sample	I	II	III	IV	V
Time	Control	0	10	20	20
Radioactivity	2.28	2.26	2.29	2.34	0.0

The results of these three experiments indicate that under the given conditions there is, within the experimental error, no interchange of oxalate between chromioxalate ion and oxalate ion in solution.

Discussion

If the mechanism of the racemization of optically active chromioxalate ion involves an ionization step with subsequent recombination, then the rate of the inversion (not of the racemization, which is double that of the inversion) of optically active chromioxalate ion should deter-

(7) Penick, Rev. Sci. Instruments, 6, 115 (1935).

(8) Livingston and Bethe, Rev. Modern Phys., 9, 245 (1937).

mine the rate of interchange of the oxalate in chromioxalate ions with added oxalate ions. If, however, the racemization does not involve an ionization then the rates of the inversion and interchange can be widely different. At a temperature of 35° the half-time for the inversion of *d*-chromioxalate ion has been calculated to be about twenty-four minutes. If the inversion of configuration of chromioxalate ion is paralleled by an interchange with oxalate ion in solution, then in a solution containing 0.06 molar chromioxalate ions and 0.012 molar radioactive oxalate ions, the radioactive oxalate should show a loss in radioactivity due to interchange alone of well over 50% in twelve minutes and of over 80% in twenty-five minutes. The results given in Tables I and II show that there is probably no loss in radioactivity after twenty-five minutes or, at most, only a very slight loss. This seems to indicate rather clearly that the mechanism of the racemization does not involve an ionization step.

To explain the racemization the only alternative at present seems to be some sort of intramolecular rearrangement. A plausible scheme is the one proposed by Werner[9] in his original re-

(9) Werner, *Ber.*, **45**, 3061 (1912).

port on optically active potassium chromioxalate. Werner suggested that the racemization might involve the breaking of only one of the bonds of one of the oxalate ions. The resulting pyramidal structure could then undergo an inversion of configuration and eventually give a racemic product. This is, however, only one of several possible mechanisms, and the available information does not seem to allow a choice to be made. It is hoped that a kinetic investigation of the racemization reaction will throw more light on this interesting question.

Conclusion

The interchange of oxalate ions with chromioxalate ions in aqueous solution has been investigated with the use of radio-carbon. At a temperature of 35° the exchange of oxalate ions is negligibly small. This result indicates that the racemization of the optically active chromioxalate ion, which under the same conditions is quite rapid, does not take place by a mechanism which involves an ionization of the coördination complex.

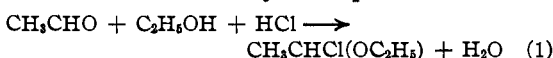# The Preparation of α-Alkyl-β-alkenylacetylenes[1]

BY W. F. ANZILOTTI AND R. R. VOGT

Introduction

α-Alkyl-β-vinylacetylenes have been prepared by Carothers and Jacobson[2] through the interaction of the sodium salt of monovinylacetylene and alkyl bromides in liquid ammonia. Truchet[3] prepared α-allyl-β-amylacetylene by the reaction of allyl benzenesulfonate with the sodium salt of 1-heptyne. Merling[4] obtained compounds of the type $CH_2\!\!=\!\!C(R)C\!\!\equiv\!\!CH$ in the desaturation of acetylenic carbinols prepared by the condensation of sodium acetylide and ketones. The preparation of compounds of the type $RCH\!\!=\!\!CH\!\!-\!\!C\!\!\equiv\!\!CH$ was not satisfactory due to poor yields of the acetylenic carbinols resulting from

(1) Paper XXX on the chemistry of the alkylacetylenes and their derivatives; previous paper, THIS JOURNAL, **60**, 2882 (1938).
(2) Jacobson and Carothers, *ibid.*, **55**, 1622 (1933).
(3) Truchet, *Compt. rend.*, **191**, 854 (1930).
(4) Merling, Farbenfabriken vorm. F. Bayer and Co., German Patent 290,558; *Friedl.*, **12**, 61.

the condensation of sodium acetylide and aldehydes. Lespieau and Guillemonat[5] obtained divinylacetylene by the action of zinc dust on 1,6-dibromo-2,5-diethoxy-3-hexyne.

Dykstra, Lewis and Boord[6] have shown that α,β-dibromoethyl ethers react with alkylmagnesium bromides to give the corresponding β-bromo ethers, which, upon desaturation with zinc dust, give fair yields of olefins. The present paper is concerned with the reactions of alkynylmagnesium bromides and α,β-dibromoethyl ethers and subsequent desaturation of the resulting β-bromoalkynyl ethers, to give the corresponding α-alkyl-β-alkenylacetylenes. The syntheses can be shown by the equations

$$CH_3CHO + C_2H_5OH + HCl \longrightarrow$$
$$CH_3CHCl(OC_2H_5) + H_2O \quad (1)$$

(5) Lespieau and Guillemonat, *Compt. rend.*, **195**, 245 (1932).
(6) Dykstra, Lewis and Boord, THIS JOURNAL, **52**, 3396 (1930).