

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF  
MANITOBA]

## THE VELOCITY AND MECHANISM OF RACEMIZATION. I. ROCHELLE SALT

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The so-called catalytic racemization in presence of caustic alkali or strong acid is a process which has received very little attention from the physico-chemical point of view. Walker<sup>1</sup> studied the velocity of racemization of amygdalin and found it to comply with the formula of a unimolecular reaction. Extensive measurements of the velocity of racemization of tartaric acid and mandelic acid are due to Winther.<sup>2</sup> He finds the reaction to be unimolecular in both cases, but his method of experiment leaves something to be desired. Realizing that the decrease in the rotation of tartaric acid or its salts might be due to the formation of either racemic or meso form or both, he thought it necessary to acidify the alkaline solution after heating and carry out a laborious analysis for the two forms. From our experience of this method we have concluded it to be hopelessly inaccurate. Indeed, Winther himself in certain cases incorporates truly enormous correction factors, which render the method undesirable. By this method of experiment too he overlooked what we consider an important factor, *viz.*, the change in the sign of rotation in strong alkali.<sup>3</sup> It is somewhat remarkable that the ordinary student preparation of racemic acid from *d*-tartaric acid is really a racemization from the levo side.

With regard to the mechanism of racemization, even less has been done. McKenzie and Thompson<sup>4</sup> attribute racemization to direct interchange of the groups attached to the asymmetric carbon atom, but they find racemization by alkali inexplicable. Rothe<sup>5</sup> attributes racemization to a mobile hydrogen atom, tautomerism and racemization being analogous processes. This being the state of affairs, we thought it advisable to repeat and extend the work of Winther.

When we consider the possible mechanisms in virtue of which tartaric acid becomes inactive, it seems surprising that the formula for a unimolecular reaction should ever have been complied with. As soon as *l*-tartrate forms, a back reaction of equal velocity constant sets in. The differential equation for the velocity is therefore

$$\begin{aligned} dx/dt &= k(a - x) - kx \\ &= k(a - 2x) \\ \therefore k &= 2.3/2t \log_{10} a/(a - 2x) \end{aligned}$$

<sup>1</sup> Walker, *J. Chem. Soc.*, **83**, 472 (1903).

<sup>2</sup> Winther, *Z. physik. Chem.*, **56**, 465-511 (1906).

<sup>3</sup> Cf. *Nature*, **129**, 281 (1932).

<sup>4</sup> McKenzie and Thompson, *J. Chem. Soc.*, **87**, 1004 (1905).

<sup>5</sup> Rothe, *Ber.*, **47**, 843 (1914).

If  $\alpha_0$  is original rotation,  $\alpha_t$  is rotation after time  $t$ , then

$$\begin{aligned}\alpha_0 &\propto a \\ \alpha_t &\propto (a - 2x)\end{aligned}$$

Hence

$$k = 2.3/2t \log_{10} \frac{\alpha_0}{\alpha_t} \quad (i)$$

When the inactive (racemic) form begins to precipitate (as it obviously does after a certain time), the  $l$ -form will have an approximately constant concentration =  $y$ . Hence, after this stage

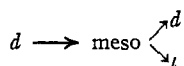
$$dx/dt = k(a - x - y)$$

If  $t'$  is time to precipitation,  $x = y$ . Hence

$$\begin{aligned}k &= 2.30/(t - t') \log_{10} (a - 2y)/(a - (x + y)) \\ \alpha_{t'} &\propto (a - 2y) \\ (\alpha_0 - \alpha_t) &\propto (x + 2y) \propto (x + y) \quad (\text{if } y \text{ is small and constant}) \\ \therefore k &= 2.30/(t - t') \log_{10} \frac{\alpha_0}{\alpha_t} \quad (ii)\end{aligned}$$

Therefore, if the process of inactivation is simply and entirely  $d \longrightarrow l$ , the formula for a unimolecular reaction should be complied with, except that the constant should have half the numerical value of the ordinary formula, in the initial stage of the reaction, after which there should be a sudden decrease in the value of the constant to half its initial value, provided the same formula is used, at the point where the solution becomes saturated with the sparingly soluble racemate. Since, however, supersaturation with racemate is likely to occur, this will reduce the suddenness of the transition.

According, however, to Winther, racemate formation takes place via the meso form, a view which stereochemical considerations would seem to favor.



Hence

$$\begin{aligned}dx/dt &= k_1(a - x) - 1/2k_2x; \\ \text{let } k_3 &= k_1 + 1/2k_2, \text{ then} \\ k_3 &= 1/t \log_e k_1 a / (k_1(a - x) - 1/2k_2x) \quad (iii)\end{aligned}$$

If  $k_2 = 0$ , this becomes the formula for a unimolecular reaction. If  $k_2$  is real, the constant calculated in accordance with the simple formula for a unimolecular reaction will increase with time. If therefore we calculate throughout with the simple formula, we may expect the following behavior. (1) The formula yields a constant value of  $k$ , decreasing, however, more or less sharply to half the initial value at a certain stage. This corresponds to  $d \longrightarrow l$  as the sole process. (2) The value of  $k$  increases steadily. This corresponds to  $d \longrightarrow \text{meso} \longrightarrow l$  as the sole process. (3) Processes 1 and 2 may be consecutive or simultaneous.

### Experimental

Preliminary experiments with different tartrates and tartaric acid heated for varying periods of time in the neighborhood of  $100^{\circ}$  convinced us that under these circumstances the acid racemization is inappreciable. We therefore decided to confine ourselves to alkaline racemization and to choose as our active tartrate sodium potassium tartrate, since this salt is cheap and readily obtained pure. The salt used was Mallinckrodt U. S. P., and the sodium hydroxide Mallinckrodt U. S. P. sticks. Although the solutions of sodium hydroxide were not made up from metallic sodium, they were almost entirely free from carbonate, a fact which is eventually to be attributed to the extreme dryness of the climate in central Canada.

The apparatus for the velocity measurements was constructed of Pyrex glass and consisted of two concentric chambers. The inner chamber was furnished at the top with a ground-in Pyrex condenser and at the bottom with a capillary neck and stopcock. The outer jacket had side inlets like a condenser, but flush with the bottom and top to prevent dead space. The side arms were connected by pressure tubing to a circulating pump and boiler. The pump was driven on the axis of an electromotor, which was run well below its maximum speed. The water in the boiler was kept vigorously boiling and the whole apparatus was heavily lagged with cotton wool and asbestos. In this way it was possible to keep the temperature constant at  $96.2^{\circ}$  within  $0.1^{\circ}$ . The temperature was read through a telescope focused on a small Anschütz thermometer suspended in the inner chamber, a small window being left in the lagging for this purpose. To conduct an experiment 0.1 mole of Rochelle salt ( $0.1 \text{ NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O} = 28.22 \text{ g.}$ ) was dissolved in the appropriate sodium hydroxide solution and made up to 100 cc. In the meantime the motor was started and, when the temperature had risen to its constant value of  $96.2^{\circ}$ , the inner chamber was filled with solution up to a mark on the constricted neck. The time of commencement was taken as the time at which the thermometer rose to  $96.2^{\circ}$  after introduction of the solution. After the lapse of one hour, in the first case, the solution was run into a buret tube packed at the bottom with glass wool, and immediately cooled under the tap, the time of completion of the run being taken as the mean of the time of cooling. After determination of the rotation of the solution, it was returned to the apparatus, any slight loss due to evaporation being made up by addition of water; with a ground-in condenser this loss was extremely small. All apparatus was washed out with solution so that there was no loss in volume due to adhering to the sides of the apparatus. The rotations were read in a Hilger 3-field polarimeter, using a 2-dcm. tube. An accuracy in reading of  $0.01^{\circ}$  was always obtained, although the stronger solutions required filtration through asbestos to obtain the necessary brightness.

The hydroxyl-ion concentrations of all solutions were determined after dissolving the (hydrated) Rochelle salt. Considerable difficulty was experienced in finding a suitable electrode for the strongly alkaline solutions containing Rochelle salt; the hydrogen electrode gives wavering and uncertain values in strongly alkaline solutions of Rochelle salt. Eventually, the manganese hydroxide electrode was found to give good comparative values between caustic soda solutions and solutions of Rochelle salt in caustic soda. A method based on the saponification of ethyl acetate also gave fair results in the less alkaline solutions, but failed at higher concentrations, owing to the increasing insolubility of the ethyl acetate. All methods, however, without exception, indicated that the hydroxyl-ion concentration in the solutions containing Rochelle salt was distinctly lower than that in the corresponding sodium hydroxide solution alone. We consider this good qualitative evidence of the formation of a complex between the Rochelle salt

and hydroxyl ions. Table I contains a selection of the results to indicate the magnitude of the differences observed.

HYDROXYL-ION CONCENTRATIONS		
Strength of NaOH, <i>N</i>	(OH) of NaOH, <i>N</i>	(OH) of solution, <i>N</i>
1.07	0.775	0.110
1.907	1.350	0.368
2.93	1.965	1.3
3.66	2.54	1.5
5.16	3.075	1.8
6.97	3.059	2.02
9.36	2.807	1.88

**Velocity Constants.**—The method of determining these was to plot the observed rotations against time, draw a smooth curve through the points and calculate the constants for each hour. For the purpose of comparison with Winther's figures, we have used his formula  $k = 100/t \log_{10} (\alpha_0/\alpha_t)$ .

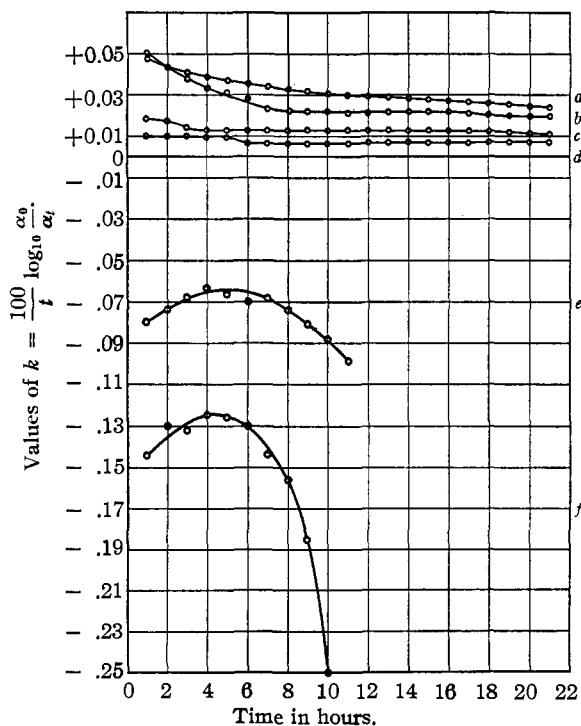


Fig. 1.—(a), 6.97 *N* NaOH; (b), 5.16 *N* NaOH; (c), 3.66 *N* NaOH; (d), 1.907 *N* NaOH; (e), 9.36 *N* NaOH; (f), 13.8 *N* NaOH.

The results are embodied in Fig. 1, where the values of  $k$  are plotted against time; the constants for the levorotatory solutions (see below) are given

negative values and this accounts for the inversion of the curves pertaining to 9.36 *N* and 13.8 *N* NaOH.

**Specific Rotations of Rochelle Salt in Sodium Hydroxide.**—As we used sodium hydroxide solutions of increasing strength we observed that the initial rotation dropped more and more, that is, that the specific rotation became less and less. We thought it advisable therefore to carry out a complete series of measurements of the rotation of (cold) solutions of Rochelle salt in sodium hydroxide; the solutions were always molar with respect to Rochelle salt. Unfortunately, our polarimeter was not fitted with a monochromator, so we were obliged to use a series of light filters. The filters were Wallace color filters and had the following transmissions.

Transmissions, Å.	Filter number				
	2	3	4	5	6
	7608-6100	7608-5800	7608-5400	7608-5300	7608-5000

For analytical purposes, filter 3 was used throughout. The results are given in Table II.

TABLE II  
SPECIFIC ROTATIONS OF MOLAR ROCHELLE SALT (ANHYDROUS) IN SODIUM HYDROXIDE  
OF VARYING CONCENTRATION

Strength of NaOH, <i>N</i>	Specific rotation at 22.2°				
	2	3	4	5	6
0.0 (water)	25.2	26.8	28.1	28.5	28.5
1.10	23.3	25.2	26.3	26.8	27.1
1.907	21.7	22.9	24.0	24.4	24.5
2.72	19.7	20.8	21.7	22.1	22.1
5.16	13.1	13.7	14.4	14.8	14.9
6.97	6.68	6.99	7.2	7.4	7.5
9.36	-0.43	-0.91	-1.12	-1.22	-1.26
14.18	-10.9	-12.0	-12.7	-12.7	-12.8

The 14.18 *N* sodium hydroxide solution of Rochelle salt preserved its rotation unchanged over the week-end. There is therefore no question of progressive racemization at room temperature. The two levorotatory solutions were acidified, when potassium hydrogen tartrate precipitated. This was redissolved in water and the rotation taken; the rotation of the acidified mother liquor was also taken. Both were dextrorotatory. From the observed dextro rotations the corresponding amount of *d*-Rochelle salt was calculated. This was always much less than the original, in other words, considerable racemization had taken place simply as a consequence of dissolving the Rochelle salt in cold sodium hydroxide. In the case of the 9.36 *N* solution, the cold racemization amounted to 16% and of the 14.18 *N* to 83%.

### Discussion

The form of the *k*-curves for solutions of sodium hydroxide concentration ranging from 1.097 *N* to 6.97 *N*, considered in the light of the theoretical considerations previously laid down, leads to the conclusion that in these

strengths of alkali, the process is direct formation of racemate, accompanied by slight meso formation. When the curves are drawn on a larger scale, a slight upward trend of the constants is observable, after the fall to half value, corresponding to the process, dextro  $\rightarrow$  meso  $\rightarrow$  levo. It is possible that in the above concentrations of alkali, the process is that given.

It has already been remarked that in alkali concentrations greater than 9 *N*, the solution is levorotatory, and the *k*-curves for these cases are distinct from the others. It seems reasonable to attribute this phenomenon to the formation of a levorotatory complex between the Rochelle salt and the sodium hydroxide, or rather hydroxyl ions. The measurements of hydroxyl concentration bear this out. The experiments on acidification of the levorotatory solutions show that the instantaneous formation of the complex has already accomplished a large part of the racemization. As an instance of the puzzling nature of the phenomena here, it may be observed that whereas the 9.36 *N* solution had become completely inert in ten hours, the 13.8 *N* solution was still distinctly levorotatory after twelve hours of heating.

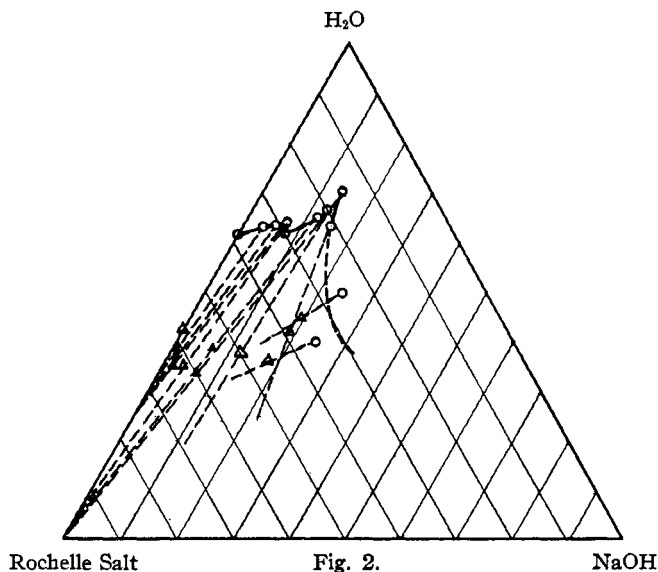
If we assume that an equilibrium is established in cold solution between levorotatory complex and dextrorotatory Rochelle salt, and that racemization takes place via the complex, we can still introduce an appearance of reason into these intricate results, as follows. The process whose velocity is measured on heating is a slow change of levorotatory complex into inactive complex, the decrease in concentration of levo complex being made up by transformation of residual dextro into levo complex. Alternatively, the change of levo complex into inactive tartrate can be brought about instantaneously by acidification. All this may seem far fetched, but the following experimental facts have to be met.

1. There is definite experimental evidence of the formation of a complex.
2. "Acid racemization" (instantaneous and in the cold) is more nearly complete in 13.8 *N* sodium hydroxide.
3. "Heat racemization" is more rapid in 9.36 *N* sodium hydroxide than in 13.8 *N*.

Evidence of the sufficiency of our experimental technique is afforded by a study of the racemization of mandelic acid, which we have just completed. Here, both acid and alkaline racemization yield true constants by the unimolecular formula, and there is no evidence of complex formation, or change of sign of rotation. The drift of the constants is peculiar to Rochelle salt, *i. e.*, presumably, to tartrates.

The assumption of complexes in optically active solutions is by no means new, but, so far as the authors are aware, no definite experimental evidence for their existence has yet been brought forward. As our hypothesis, though not our facts, depends on the demonstration of the existence of such a complex, we decided to carry out a phase rule study of the system sodium

hydroxide-Rochelle salt-water. This was done, using Schreinemaker's method. The method cannot, of course, yield definite information where one of the components undergoes decomposition, that is, when it ceases to be a component at all, but the form of the curves should indicate whether or not complex formation takes place. The solubility determinations were carried out in a thermostat at 25°, using a technique described elsewhere.<sup>6</sup>



We were unable to carry the observation beyond 8 *N* sodium hydroxide, because at this concentration the solid phase becomes a glutinous mass impossible to filter. The solubility curve shows three distinct portions, the first of which corresponds to Rochelle salt hydrated, the second to anhy-

TABLE III  
SOLUTIONS IN EQUILIBRIUM SOLID PHASE

Expt.	Liquid phase			Solid phase		
	Rochelle salt, %	NaOH, %	H <sub>2</sub> O, %	Rochelle salt, %	NaOH, %	H <sub>2</sub> O, %
1	39.0	..	61.0	58	..	42
2	33.3	3.7	63.0	61	1.7	37.3
3	31.0	5.8	63.2	61.8	1.7	36.5
4	29.0	7.3	63.75	62.5	2.6	34.9
5	29.5	7.6	62.9 <sup>6</sup>	61.7	3.9	34.4
6	20.2	13.5	66.3	60.0	6.8	33.2
7	22.6	12.2	65.2	54.7	7.2	38.1
8	16.1	13.85	70.05	50.0	12.5	37.5
9	21.6	15.3	63.1	39.6	19.0	41.4
10	35.2	24.8	40.0	45.3	18.9	36.8
11	25.7	23.9	50.4	36.9	19.4	43.7

<sup>6</sup> Campbell and Yanick, *Trans. Faraday Soc.*, in press.

drous Rochelle salt, and the third we tentatively suggest corresponds to solid complex. At all events, the tie-lines show no indication of running to the sodium hydroxide corner. For the reason previously given, it cannot be expected that the tie-lines should intersect in a point. The appearance of the solid phase at this stage is remarkable. It swells in bulk so as to occupy almost the total volume and resembles a stiff gel. The numerical results are contained in Table III.

The triangular diagram is interesting and has therefore been reproduced.

It is hoped shortly to communicate similar work which has been done on camphoric acid and substituted tartaric acid. Work is now proceeding on the acid and alkaline racemization of mandelic acid.

### Summary

The process of inactivation of Rochelle salt when heated with sodium hydroxide has been investigated mathematically. Measurements of the velocity of inactivation have been made in a special apparatus. The drift of the constants is interpreted in the light of the equations deduced. The interpretation is rendered difficult by the fact that a levorotatory complex is formed, but the matter is discussed at length. Experimental evidence for the existence of the complex, depending on (1) sign of rotation, (2) hydroxyl-ion concentration and (3) a phase rule study of the system Rochelle salt-H<sub>2</sub>O-NaOH, is also adduced.

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[CONTRIBUTION FROM THE RYERSON PHYSICAL LABORATORY, UNIVERSITY OF CHICAGO]

## THE ATOMIC ARRANGEMENT IN GLASS

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### 1. Introduction

It must be frankly admitted that we know practically nothing about the atomic arrangement in glasses. Glasses are described as supercooled liquids or as solids. The former term is justifiable from the point of view of physical chemistry, the latter from the theory of elasticity. It seems rather futile, however, to try to decide which of the two descriptions is the proper one to use, when we are ignorant about the characteristic properties of the atomic arrangement.

It has been said that the x-ray diffraction patterns obtained from glasses indicate that glasses consist of crystalline material.<sup>1</sup> It is claimed, for example, that the main features of the diffraction pattern of vitreous silica can be accounted for on the following basis: (1) vitreous silica consists of cristobalite crystallites; (2) the average linear dimension of the crystallites

<sup>1</sup> J. T. Randall, H. P. Rooksby and B. S. Cooper, *Z. Krist.*, **75**, 196 (1930).