

recent work of the writer, and of London, which allowed an approximate calculation for large perturbations. It was still found that the probability that hydrogen should deactivate an activated molecule was such as to be consistent with the assumption that an activated molecule is deactivated every time it hits an unactivated molecule of the same kind, within a factor of around ten (this conclusion being drawn after a discussion of experimental results which give the relative probability that a hydrogen molecule and an unactivated molecule of the same kind will deactivate the activated molecule).

The various factors which affect the probability of transfer of energy have also been investigated. It was found that, in general, increasing the frequency of the oscillator decreases the probability, increasing the force constant of the oscillator decreases the probability, increasing the "sharpness" of the collision (*i. e.*, the steepness with which the force between the oscillator and the colliding particle goes up as they approach) increases the probability, and increasing the mass of the colliding particle decreases the probability. The latter effect was of interest in connection with the observed difference between hydrogen and helium, and a study was made of the effect of the mass of the colliding particle when other things were varied. However, on account of various complications, it was not possible to decide whether the observed difference between hydrogen and helium actually found a complete explanation in the calculated results.

Note added in proof, Oct. 17, 1932.—Since this article was submitted Jackson and Mott, Ref. 10, have shown how to solve the differential equation 3 and evaluate the integral in (10), for the particular case, $\rho = 1$, when u_{nn} is left in the exponential form instead of being put in the form (13). A few rough calculations made from their formula seem to show about as satisfactory agreement with Table III as is shown between Tables I and II.

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THE VELOCITY AND MECHANISM OF RACEMIZATION. II. MANDELIC ACID

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As a continuation of the work described in Part 1,¹ we have investigated in a similar manner the racemization of mandelic acid in the presence of acid and alkali. The apparatus and methods are described in Part 1.¹ We chose mandelic acid in contrast to Rochelle salt, because the mechanism must necessarily be simpler, in so far as there is no possibility of meso formation. We supposed, as a result of our work already described, that complex formation was a necessary condition of racemization, but we have

¹ Campbell and Campbell, THIS JOURNAL, 54, 3834 (1932).

found no experimental evidence of the existence of a complex in the case of mandelic acid, although the existence of a very loose complex is not excluded.

The *l*-mandelic acid was prepared from amygdalin by a method described elsewhere.²

Rotatory Power.—The specific rotations of mandelic acid in acid and in alkali were first determined, as described in Part I. Light filter No. 3 was used (transmission: 7608–5800 Å.) and the temperature of measurement was 26.5°. In view of the cost of amygdalin all solutions used in this work were decimolar with respect to mandelic acid. The results are contained in Table I.

TABLE I
SPECIFIC ROTATIONS OF DECIMOLAR MANDELIC ACID IN VARIOUS MEDIA

Medium		Medium	
11.24 <i>N</i> HCl	–159°	Water	–129°
4.49 <i>N</i> HCl	–145	0.935 <i>N</i> NaOH	–106
2.38 <i>N</i> HCl	–140	1.97 <i>N</i> NaOH	–107
1.25 <i>N</i> HCl	–136	2.72 <i>N</i> NaOH	–113
Water	–128	6.97 <i>N</i> NaOH	–113

It is apparent that the rotation of mandelic acid passes through a minimum in about 1 normal sodium hydroxide, after which it increases only very slightly. In alkaline media we are dealing principally with the mandelate ion, the concentration of which will decrease slightly with increasing concentration of sodium hydroxide. In acid solution the mandelic acid will be present almost entirely as non-dissociated molecules. Perhaps one might say that there is no indication of complex formation in the alkaline solutions, but some indication of it in the acid solutions.

H⁺ and OH[–] Concentrations.—The H⁺-ion concentrations were determined, in acid by means of the quinhydrone electrode, in alkali by means of the manganese hydroxide electrode. The combinations

Hg/Hg₂Cl₂ in satd. KCl/HCl/Quinhydrone

and

Hg/Hg₂Cl₂ in satd. KCl/0.1 *M* Mandelic acid in HCl/Quinhydrone

yielded identical e. m. f.'s throughout, as did the combinations

Hg/Hg₂Cl₂ in satd. KCl/NaOH/Manganese hydroxide

and

Hg/Hg₂Cl₂ in satd. KCl/0.1 *M* Mandelic acid in NaOH/Manganese hydroxide

There is no evidence of complex formation from this source.

Conductometric Experiments.—The molecular conductivity of *M*/10 sodium mandelate was determined, in the usual manner, together with the molecular conductivities of 2.72 *N* sodium hydroxide, 6.97 *N* sodium hydroxide, and 11.24 *N* hydrochloric acid. Decimolar *l*-mandelic acid

² *Trans. Faraday Soc.*, **26**, 561 (1930).

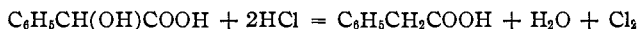
was then dissolved in each of these three media and the molecular conductivity again determined. No special precautions were taken in the work. The measurements were made in a thermostat at 25°. The experimental value for "medium + $M/10$ mandelic acid" (column 3) was compared with the sum of the molecular conductivity of the sodium hydroxide medium alone and the conductivity of the fraction of a mol of sodium mandelate contained in a volume which contained one mol of sodium hydroxide (column 4). The results are contained in Table II.

TABLE II

Nature of medium	μ obs.		μ for medium + μ for $M/10$ m. a.	Difference	Ratio
	Medium alone	Medium + $M/10$ m. a.			
Water	...	48(NaM)
2.62 N NaOH	158	166	160	-6	1.04
6.97 N NaOH	106	95	107	12	0.89
11.24 N HCl	44.5	44	45	1	.98

The deviation from additivity is hardly sufficient to indicate complex formation.

Velocity of Racemization.—The apparatus and method of work are described in Part 1.³ At the temperature of experiment (96.2°) no racemization could be detected in acid solutions of strength below 11.24 N hydrochloric acid. When working with mandelic acid in 11.24 N hydrochloric acid (concentrated acid) it was observed that the solution developed a distinct yellow-green color, together with a pronounced smell of phenylacetic acid. It was thought that decomposition had taken place in the sense of the equation



This was tested for by taking a measured volume of the solution after a series of racemization measurements, adding potassium iodide and titrating the liberated iodine with standard thiosulfate. In two such experiments the results corresponded to 10.4 and 6.9% decomposition, respectively, an amount insufficient to account for the total decrease in rotation, but amounting to a considerable fraction of it. The only method of correcting for this decomposition which occurred to us was to take the mean of the two results (8.65%), multiply the differences between the zero reading and subsequent readings by 0.0865 and add this to the experimental reading. Correcting in this way, and graphing the results in the manner previously described, series of k values are obtained which are reproduced in Fig. 1. The k value curves for $M/10$ mandelic acid in 0.935, 1.97, 2.72 and 6.97 N sodium hydroxide are also given.

It should be observed that the greater solubility of r -mandelic acid as compared with that of l -mandelic acid obviates certain complications

³ THIS JOURNAL, 54, 3834 (1932).

which were to be expected in the case of tartrate racemization. An inspection of the curves shows that racemization of mandelic acid in alkali is much more rapid than in acid, and that in both cases it is much more rapid than with Rochelle salt. A more detailed examination shows that in the case of the acid racemization the velocity "constant" is strictly a constant for the first eleven hours of heating, after which it shows a small but steady decrease, possibly connected with the decomposition of the mandelic acid.

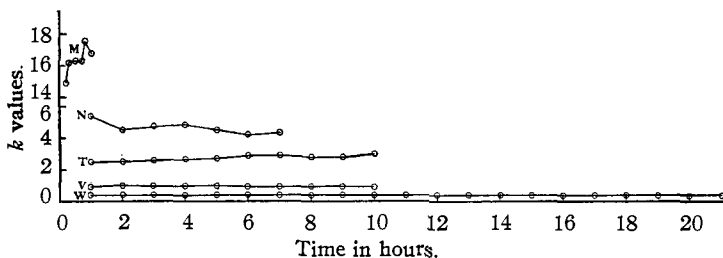
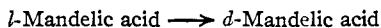


Fig. 1.—M, 6.97 *N* NaOH; N, 2.72 *N* NaOH; T, 1.92 *N* NaOH; V, 0.935 *N* NaOH; W, 11.24 *N* HCl.

In the alkaline solutions, the deviations are irregular and presumably due to experimental error. It was not possible to carry out measurements in alkali of higher concentrations, because, first, mandelic acid became sparingly soluble in, for instance, 9 *N* sodium hydroxide, and, second, because the velocity became inconveniently great: in 6.97 *N* sodium hydroxide, racemization is complete after little more than an hour's heating. We conclude that the process of racemization of mandelic acid, in both acid and in alkali, is simply represented by the equation

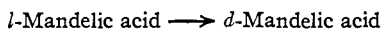


Attempts to Isolate a Complex.—On the basis of our supposition that racemization was necessarily preceded by formation of a complex, we made attempts to isolate the supposed complex between mandelic acid and hydrochloric acid. In the first place we evaporated a solution of mandelic acid in concentrated hydrochloric acid to dryness in a stream of hydrogen chloride, in a weighed dish. Nothing but mandelic acid was obtained. In the second place an all-glass system was built up consisting of a flask containing dry mandelic acid connected to a hydrogen chloride generator and closed manometer. On forcing in hydrogen chloride gas, the pressure rose progressively to two atmospheres, when the experiments were discontinued, without indication of a rest point. These experiments likewise yield no evidence of complex formation.

Summary

The velocity of racemization of mandelic acid in hydrochloric acid and in sodium hydroxide has been studied, using an apparatus previously de-

scribed. The variations in the constant are purely sporadic. Mandelic acid racemizes much more readily in sodium hydroxide solution than in acid solution, and in both much more readily than Rochelle salt. There is nothing to show that the racemization of mandelic acid is any other than is represented by the simple scheme



The existence of a complex has been investigated by the methods of hydroxyl-ion concentration and by measurements of conductivity but neither method gives any certain indication of complex formation. Attempts to isolate a complex have failed. It is shown that the racemization of mandelic acid in strong hydrochloric acid is accompanied by a certain amount of decomposition, together with liberation of free chlorine: possibly the decomposition product is phenylacetic acid.

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[CONTRIBUTION FROM THE ALABAMA EXPERIMENT STATION]

QUANTITATIVE DETERMINATION OF CALCIUM BY THE MAGNETO-OPTIC METHOD

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Allison and Murphy have described a magneto-optic¹ method of chemical analysis in which compounds are detected by characteristic light minima produced by the time lag of their Faraday effect. Since very minute traces of a compound will produce its characteristic minima regardless of what other substances may be present, it seemed desirable to study the quantitative possibilities of this method.

Technique.—In general, the method consists of finding the smallest amount of material that will produce light minima characteristic of a calcium compound. This will represent a definite concentration of calcium which is determined by using solutions of known concentration and, from this, the amount in an unknown sample is calculated.

The water used is redistilled from Pyrex glass apparatus. Great care is exercised to guard against any possible contamination. Standard volumetric apparatus is used.

The fact that some calcium is dissolved from glass is recognized. The water was always tested before making an analysis and consistently gave no calcium minima. The reproducibility of results and checks with permanganate titration indicate that the amount dissolved is either negligible or constant.

To test the rate of solution of calcium from glass, water redistilled from Pyrex was left standing in a Pyrex beaker under a bell jar and in a 100-cc. normax flask and tested from day to day for calcium chloride. To ensure the presence of chloride without the addition of any calcium the water was exposed to fumes from concentrated hydrochloric acid. The water in the normax flask gave negative results until the fifth day, when the

¹ Allison and Murphy, *THIS JOURNAL*, **52**, 3796 (1930).