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## The Kinetics of Acid-catalyzed Esterification of Cyclohexanedicarboxylic Acids

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The acid-catalyzed esterification of cyclohexanedicarboxylic acid has been studied previously.<sup>1</sup> It was shown that this compound behaved more like isobutyric acid than diethylacetic acid due to the fact that the cyclohexane ring prevented the hydrocarbon chains from approaching the carboxyl group. The cyclohexanedicarboxylic acids offer further complications, since there are three sets of *cis-trans* isomers possible, and the relative rates of esterification of the possible forms will undoubtedly depend on the geometrical as well as positional arrangement of the carboxyl groups. It seemed, therefore, of interest to investigate the kinetics of esterification of such compounds.

The isomers of 1,2-cyclohexanedicarboxylic acid were first prepared by Baeyer<sup>2</sup> who assigned *cis* and *trans* structures to his compounds. This assignment was confirmed by Werner and Conrad,<sup>3</sup> who resolved the *trans* isomer into optically active forms.

The 1,3-cyclohexanedicarboxylic acids were first prepared by Perkin,<sup>4</sup> who assigned structures on the basis of anhydride formation. This assignment was confirmed by Böeseken and Peek<sup>5</sup> by resolution of the optical isomers of the *trans* form.

The isomers of 1,4-cyclohexanedicarboxylic acid were first prepared by Baeyer<sup>6</sup> and structural assignments made on the basis of physical properties. Mills and Keats<sup>7</sup> confirmed these designations on the basis of optical activity. It thus appears that the structures of all of these isomers are well established, and that interpretation of esterification results on a structural basis is possible.

## Experimental

The starting materials for preparation of the various cyclohexanedicarboxylic acids were the purified phthalic acids. These were hydrogenated in the form of the acids or methyl esters using Adams platinum catalyst, acetic acid solvent, and 50–60 p. s. i. hydrogen pressure.

The *cis*-1,2 acid precipitated when the mixture resulting from the hydrogenation of phthalic acid was cooled to 20°. It was recrystallized three times from acetic acid and once from water. The *trans* form was obtained by refluxing a mixture of 50 g. of the crude hydrogenated acid with 100 ml. of water and 170 ml. of concd. sulfuric acid, for a period of twenty-four hours, after which the mixture was cooled overnight. The crystals which separated were filtered, washed, and dried. The crude product was treated for ten minutes with boiling xylene. The xylene was decanted while hot, and this treatment re-

peated twice. The remaining crystals were washed with cyclohexane, and recrystallized twice from water. A 44% yield of pure *trans*-1,2-cyclohexanedicarboxylic acid was obtained.

The *cis*-1,3 acid was recovered from the appropriate hydrogenation mixture by filtering, evaporating the acetic acid solvent, and recrystallizing the solid three times from water. A considerable quantity of the *trans* isomer was present in the solid, so that only 30% of the pure *cis* acid was recovered.

The *trans*-1,3 acid was prepared from the mixed 1,3-acids resulting from hydrogenation of isophthalic acid. The mixture was neutralized, then treated with silver nitrate and methyl iodide to form the dimethyl esters. These were fractionated in an eight-foot Vigreux column (26 theoretical plates) at a pressure of 20 mm. The first fraction, distilling between 141 and 142°, was collected, and the acid recovered by treatment with sodium hydroxide and acid. The solid product was recrystallized twice from water. Twenty-five grams of pure *trans*-1,3-cyclohexanedicarboxylic acid was obtained from 100 g. of the mixed acids.

The *cis* and *trans* forms of 1,4-cyclohexanedicarboxylic acid were prepared by hydrogenation of the dimethyl ester of terephthalic acid and subsequent conversion to the saturated acid. The mixture of *cis* and *trans* forms was refluxed with toluene (25 ml. per gram of solid) for thirty minutes, and the solid residue removed by filtration. Pure *trans*-1,4-cyclohexanedicarboxylic acid was obtained by three recrystallizations of this solid from water. The filtrate from the toluene extraction was treated with activated charcoal, filtered hot, cooled to 50°, and quickly re-filtered. The crystals obtained were again dissolved in boiling toluene, and allowed to crystallize at 50°. The resulting solid was fractionally crystallized from water, thus yielding pure *cis*-1,4-cyclohexanedicarboxylic acid. From 150 g. of the *cis* and *trans* mixture, 23 g. of pure *cis* and 75 g. of pure *trans* acids were obtained.

In order to prepare the monomethyl ester of *cis*-1,2-cyclohexanedicarboxylic acid, the corresponding ester of phthalic acid was prepared by the method of Vavon and Peignier.<sup>8</sup> This ester was then hydrogenated in the usual manner and the product recrystallized twice from petroleum ether.

The monomethyl ester of *trans*-1,2-cyclohexanedicarboxylic acid was obtained from the purified acid by treatment with acetyl chloride and conversion of the resulting anhydride to the ester by reaction with methanol.<sup>8</sup> The solid product was recrystallized from petroleum ether.

The monomethyl ester of *cis*-1,3-cyclohexanedicarboxylic acid was also prepared from the purified acid by conversion to the anhydride and subsequent reaction with methanol. The oily precipitate was recrystallized three times from petroleum ether. Table I gives melting points and assay values for the acids and monomethyl esters.

The dry methanol for esterification runs was prepared by careful fractionation of du Pont or Carbide and Carbon methanol through an eight-foot Vigreux column. Methanol-hydrogen chloride solutions were prepared as in previous work.<sup>9</sup> The method for obtaining rate constants was essentially the same as that previously reported. Corrections were made for solvent expansion as well as for the volume change caused by solution of the solid acid in the methanol. Titrations were made using carbonate-free sodium hydroxide and a mixed thymol blue-phenolphthalein indicator. The initial concentration of organic acid was usually 0.5 M, while that of HCl catalyst was 0.005 M.

- (1) Smith and Levenson, *THIS JOURNAL*, **62**, 2733 (1940).
- (2) Baeyer, *Ann.*, **258**, 145 (1890).
- (3) Werner and Conrad, *Ber.*, **32**, 3046 (1899).
- (4) Perkin, *J. Chem. Soc.*, **59**, 809 (1891); Perkin and Goodwin, *ibid.*, **87**, 842 (1905).
- (5) Böeseken and Peek, *Rec. trav. chim.*, **44**, 841 (1925).
- (6) Baeyer, *Ann.*, **245**, 103 (1888); **251**, 257 (1889).
- (7) Mills and Keats, *J. Chem. Soc.*, **147**, 1373 (1935).

- (8) Vavon and Peignier, *Bull. soc. chim.*, **45**, 299 (1929).
- (9) Smith, *THIS JOURNAL*, **61**, 254 (1939).

TABLE I

MELTING POINTS AND ASSAY FOR COMPOUNDS ESTERIFIED

Cyclohexane-dicarboxylic acid or monomethyl ester	Assay, <sup>a</sup> wt. %	M. p., °C. <sup>b</sup> found	M. p., °C. lit.	Ref.
<i>cis</i> -1,2-	99.9	190.4-191.2	191.5-192.5	<i>c</i>
<i>cis</i> -1,2, mono-methyl ester	100.3	67.4-67.8	68.5-69.0	<i>d</i>
<i>trans</i> -1,2	100.1	227.2-228.0	227.0-229.0	<i>c</i>
<i>trans</i> -1,2, mono-methyl ester	100.1	94.3-95.3	95.0-96.0	<i>d</i>
<i>cis</i> -1,3	100.1	167.0-167.8	167.5	<i>e</i>
<i>cis</i> -1,3, mono-methyl ester	100.3	56.6-57.4	Unreported	
<i>trans</i> -1,3	100.3	150.5-150.7	150.5	<i>e</i>
<i>cis</i> -1,4	99.7	171.3-172.5	170-171	<i>f</i>
<i>trans</i> -1,4-	100.0	312.3-312.7	312-313	<i>f</i>
		dec.	uncor.	

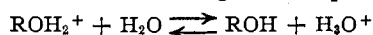
<sup>a</sup> Determined by titration with standard base. <sup>b</sup> All melting points determined in an aluminum melting point block and corrected for thermometer stem emergence. <sup>c</sup> Linstead, Davis and Whetstone, *THIS JOURNAL*, **64**, 2093 (1942). <sup>d</sup> Vavon and Peignier, *Bull. soc. chim.*, **45**, 229 (1929). <sup>e</sup> Skita and Rozzler, *Ber.*, **72**, 265 (1939). <sup>f</sup> Malachowski and Jankiewicz, *ibid.*, **67**, 1783 (1934).

### Experimental Results and Calculations

The rate constants for the acid-catalyzed esterification of organic acids may be calculated from Goldschmidt's equation

$$k = \frac{(r + n + a) \ln [a/(a - x)] - x}{(\text{catalyst})rt}$$

where  $a$  is the original concentration of organic acid,  $n$  is the original concentration of water,  $x$  is the concentration of ester formed after time  $t$ , and the catalyst for the experiments discussed here is hydrogen chloride. The constant  $r$  allows for the fact that the real reaction is between the organic acid and the complex  $\text{ROH}_2^+$ , and the concentration of the latter is affected by the presence of water formed as a product of the reaction. The water reacts with the conjugate acid of the alcohol according to the equation



and  $r$  is defined by the expression<sup>10</sup>

$$r = (\text{ROH}_2^+)/(\text{H}_2\text{O})/(\text{H}_3\text{O}^+)$$

The values of  $r$  used for methyl alcohol-water systems at 25, 35, 45 and 55° were 0.22, 0.28, 0.36 and 0.48.

For the esterification of dicarboxylic acids the Goldschmidt equation may be used directly to calculate the rate constant for reaction of the first carboxyl group provided the reaction of the second carboxyl group is negligible. Since dry methanol was used,  $n$  is equal to zero. This method of calculation was found applicable to the esterification of the first carboxyl group of

1,2-cyclohexanedicarboxylic acids only. Table II gives a sample calculation for this acid.

It has already been demonstrated that the reaction of the solvent, methanol, with the hydrogen chloride catalyst is appreciable for slow reactions at the higher temperatures used in this research.<sup>11</sup> The values for the concentration of catalyst were corrected for this reaction, and the corrected concentrations are given in the third column of Table II. The rates of reaction of the solvent and catalyst used in these calculations are those previously published.<sup>11</sup>

The rate constants for esterification of the second carboxyl group of the cyclohexanedicarboxylic acids were also calculated in this same manner when the pure monomethyl esters were used as starting materials.

TABLE II

ESTERIFICATION OF *cis*-1,2-CYCLOHEXANEDICARBOXYLIC ACID AND METHANOL AT 55°

$t$ , min.	$(a - x)$	(Catalyst) $\times 10^3$	$k \times 10^2$ liters moles <sup>-1</sup> sec. <sup>-1</sup>
0	.5053	5.00	
30	.4558	4.99	1.28
60	.4111	4.99	1.23
90	.3788	4.98	1.19
120	.3500	4.97	1.22
150	.3216	4.96	1.21
195	.2827	4.95	1.22
240	.2562	4.94	1.22
300	.2221	4.93	1.24
360	.1909	4.91	1.22
420	.1635	4.90	1.29

Average 60-360 min. 1.22

For the 1,3- and 1,4-cyclohexanedicarboxylic acids the rate of esterification of the second carboxyl group is not negligible even for the initial stages of the reaction. The total concentration of unesterified carboxyl is determined by titration with the standard alkali. Consequently the  $(a - x)$  term in Goldschmidt's equation will be represented as smaller than it would be if the second carboxyl group had not undergone any reaction, and the values for the rate constant calculated in the usual manner will increase as the reaction proceeds. When these "constants" are plotted against time, a straight line is obtained for the first 50 to 60% of the reaction. Extrapolation of this line to zero time gives the rate constant for esterification of the first carboxyl group. This is illustrated in Fig. 1. These extrapolations were made using the method of least squares.

For calculating  $k_2$ , the rate constant for esterification of the second carboxyl group of these acids, two methods were used. In some cases the monomethyl ester was prepared, and the calculations made in the standard manner. In others, the starting material was the cyclohexane-

(10) See especially Goldschmidt and Udby, *Z. physik. Chem.*, **60**, 728 (1907); Goldschmidt and Theussen, *ibid.*, **81**, 30 (1912); Goldschmidt and Melbye, *ibid.*, **143**, 139 (1929); Goldschmidt, Haaland and Melbye, *ibid.*, **148**, 278 (1929). The derivation of Goldschmidt's equation has been summarized by Smith, ref. 9.

(11) Smith, *THIS JOURNAL*, **63**, 1136 (1940);

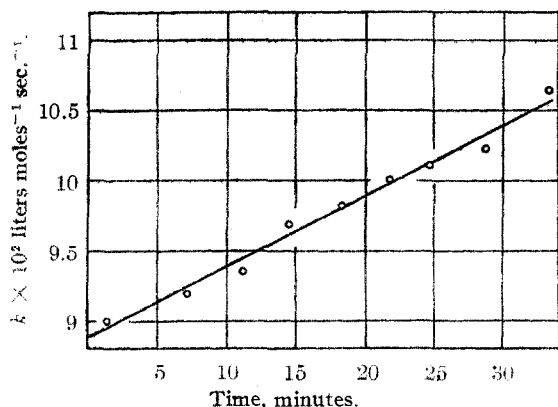


Fig. 1.—Graphical calculation of rate constant ( $k_1$ ) for esterification of *trans*-1,3-cyclohexanedicarboxylic acid at 55°: extrapolated value of  $k_1 = 8.88 \times 10^{-2}$ .

dicarboxylic acid which was allowed to react until essentially all of the first carboxyl group had been esterified. Rate constants were calculated from data taken on the remaining portion of the reaction, using a modification of the Goldschmidt equation

$$k = \frac{(2a + r) \{ \ln [a/(a - x_2)] - x_2 - \ln [a/(a - x_1)] + x_1 \}}{(\text{catalyst})r(t_2 - t_1)}$$

In this equation the usual factor  $(n + a + r)$  reduces to  $(2a + r)$  since at the start of esterification of the second carboxyl group the number of moles of water formed in the esterification of the first group will be equal to the original concentration of the dibasic acid provided the esterification takes place in two successive steps. This equation was applied by allowing the reaction to proceed until more than one equivalent of the dibasic acid had been esterified. Then samples of the reacting mixture were withdrawn and titrated at various time intervals until about 85% of the total acid groups had been esterified. Successive times were chosen as the initial time ( $t_1 = 0$ ) and rate constants based on this arbitrary zero were calculated for the remaining readings. The rate constant from the set of values of the

TABLE III

CALCULATION OF  $k_2$  FOR THE ESTERIFICATION OF *trans*-1,3-CYCLOHEXANEDICARBOXYLIC ACID AT 35°

$(a - x)$	$t_1$ min.	$k^a$	$t_2$ min.	$k^a$	$t_1$ min.	$k^a$
0.3973	0					
.3524	101	0.0132	0			
.3246	181	.0126	80	0.0118	0	
.2867	296	.0127	195	.0124	115	0.0129
.2525	429	.0124	328	.0122	248	.0123
.2215	566	.0124	465	.0122	385	.0123
.1846	779	.0121	678	.0119	598	.0119
.1557	967	.0121	866	.0120	786	.0120
Average		.0125		.0121 <sup>b</sup>		.0123
Av. deviation		.00029		.00018		.00026

<sup>a</sup> The units of  $k$  are liters moles<sup>-1</sup> sec.<sup>-1</sup>. <sup>b</sup> The figure of 0.0121 was chosen for the rate constant.

"constant" showing the smallest average deviation was chosen for the esterification reaction. An example of this type of calculation is shown in Table III.

This method for the calculation of  $k_2$  was applied to esterification of all the acids except the *trans*-1,2-cyclohexanedicarboxylic acid. This esterification was so slow that the correction for the reaction between the catalyst and solvent became too large for reasonable use, so the data were obtained using the monomethyl ester.

The rate constants for esterification of the cyclohexane-dicarboxylic acids are given in Table IV. It should be noted that the constants for esterification of the second carboxyl group of the *cis*-1,3 acid calculated using either the acid or the monomethyl ester as starting material agree very well. The agreement is not so good for the *cis*-1,2 acid, but the corrections for catalyst consumption were fairly large for this esterification, making the results obtained with the dicarboxylic acid as starting material unreliable, and probably account for the lack of closer correlation.

Figure 2 shows a plot of the logarithm of the rate constants for the esterification reactions against the reciprocal of the absolute temperature.

TABLE IV

RATE CONSTANTS AND ACTIVATION ENERGIES FOR ESTERIFICATION OF THE CYCLOHEXANEDICARBOXYLIC ACIDS

Acid	$k$	$k \times 10^2$ (liters moles <sup>-1</sup> sec. <sup>-1</sup> )				$E$ (cal. mole <sup>-1</sup> )
		25°	35°	45°	55°	
<i>cis</i> -1,2-	$k_1$	0.170	0.323	0.680	1.24	13,100
		.163	.324	.692	1.22	
	$k_2$	0.0295 <sup>a</sup>	0.0582	0.120	0.221	13,100
		.0293 <sup>a</sup>	.0590	.121	.216	
		.0282	.0538	.107	.205	
		.0293	.0562	.109	.204	
<i>trans</i> -1,2-	$k_1$	0.0774	0.170	0.336	0.632	13,500
		.0781	.171	.330	.623	
	$k_2$	0.0426 <sup>a</sup>	0.0825	0.154	0.293	12,500
		.0424 <sup>a</sup>	.0822	.158	.292	
<i>cis</i> -1,3-	$k_1$	3.05	4.78	8.78	14.6	10,300
		2.96	4.52	8.55	14.3	
	$k_2$	1.18 <sup>a</sup>	2.01	3.51	5.61	10,200
		1.17 <sup>a</sup>	1.96	3.40	5.59	
		1.15	1.99	3.39	5.36	
		1.20	1.95	3.44	5.47	10,000
<i>trans</i> -1,3-	$k_1$	1.72	3.13	5.39	8.98	10,700
		1.72	3.14	5.40	8.88	
	$k_2$	0.692	1.18	2.01	3.08	9,700
		0.695	1.21	2.00	3.10	
<i>cis</i> -1,4-	$k_1$	1.62	3.00	5.36	8.28	10,600
			3.08	5.40		
	$k_2$	0.676	1.23	1.99	3.04	9,700
			1.25	1.90		
<i>trans</i> -1,4-	$k_1$	2.80	5.06	8.71	14.4	10,400
		2.88	5.06	8.85	14.0	
	$k_2$	1.32	2.24	3.85	5.94	9,800
		1.32	2.29	3.82	5.98	

<sup>a</sup> All constants in this series determined from monoesters.

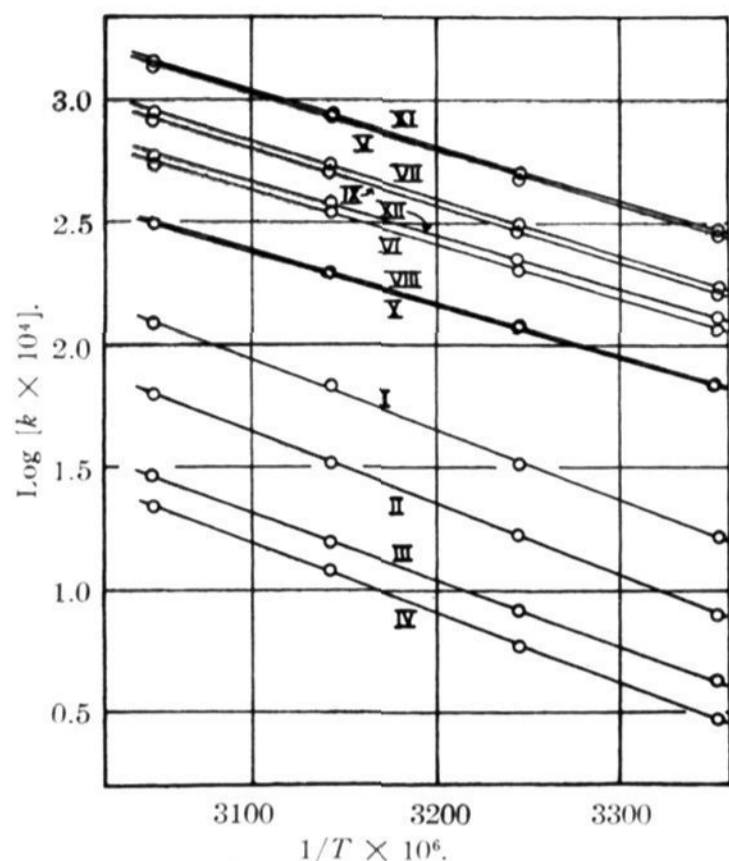


Fig. 2.—Temperature coefficients for esterification of cyclohexanedicarboxylic acids: I,  $k_1$  for *cis*-1,2; II,  $k_1$  for *trans*-1,2; III,  $k_2$  for *trans*-1,2; IV,  $k_2$  for *cis*-1,2; V,  $k_1$  for *cis*-1,3; VI,  $k_2$  for *cis*-1,3; VII,  $k_1$  for *trans*-1,3; VIII,  $k_2$  for *trans*-1,3; IX,  $k_1$  for *cis*-1,4; X,  $k_2$  for *cis*-1,4; XI,  $k_1$  for *trans*-1,4; XII,  $k_2$  for *trans*-1,4.

The activation energies included in Table IV were calculated from the slopes of these straight lines using the method of least squares.

### Discussion

An examination of Table IV shows several interesting results. As would be expected, the rate constants,  $k_2$ , for the 1,3 and 1,4 isomers, as well as the corresponding activation energies are close to those for cyclohexanecarboxylic acid. For the latter,  $k_{25}$  is  $1.18 \times 10^{-2}$  liters moles<sup>-1</sup> sec.<sup>-1</sup> and  $E$  is 10,000 cal. per mole.<sup>1</sup> The values of  $k_1$  for these acids should be, on a purely statistical basis, twice those for  $k_2$ . This seems to be the case, all  $k_1$  constants at 25° being within about 20% of twice the corresponding constants,  $k_2$ . The energies of activation for esterification of the second carboxyl group seem to be significantly lower than for the first. No explanation is apparent.

The 1,2-cyclohexanedicarboxylic acids are esterified much slower than cyclohexanecarboxylic acid. This is certainly the result of the proximity of the two acid groups. The energies of activation are also several thousand calories greater for the 1,2 acids than for the mono-substituted compound. For the *trans* form,  $k_1$  is approximately twice as great as  $k_2$ . However, for the *cis* form the value of  $k_1/k_2$  is approximately six. For this isomer the methyl group of the monoester apparently hinders esterification of the second carboxyl group.

In general, it is expected that *cis* isomers will react more slowly than corresponding *trans* forms. Table IV shows that only the 1,4 acids follow this rule. For both 1,2- and 1,3-cyclohexanedicarboxylic acids the reverse is found. However, it is interesting to note that for the 1,2 acids,  $k_1$  is greater for the *cis* isomer, but  $k_2$  is greater for the *trans* form.

In attempting to explain these results it is necessary to consider the fact that the cyclohexane ring exhibits two forms, represented by the chair and the boat configurations. In cyclohexane one may differentiate between two types of hydrogen atoms. Those extending outward from the ring are designated as equatorial while the others are known as polar.<sup>12</sup> Furthermore, at room temperatures substantially all of the cyclohexane is in the chair form, which has three polar hydrogen atoms on each side of the ring.<sup>13</sup>

Assuming the chair configuration for the cyclohexane ring, there are two possible tautomers for *trans*-1,2-cyclohexanedicarboxylic acid. One has both carboxyls in polar positions, and one has both equatorial. It would appear logical that the polar form would predominate, since here the carboxyl groups are more widely separated. There is, however, only one possible form for the *cis*-1,2 isomer, and it has one polar and one equatorial carboxyl. In a polar carboxyl, the carbonyl group is somewhat shielded, while in an equatorial carboxyl, it is relatively open to attack. Thus one would expect the first (equatorial) acid group of the *cis* form to react more rapidly than either acid group in the *trans* form. Once this equatorial carboxyl is esterified, the ester group adds to the hindrance of the remaining (polar) carboxyl, while this is not the case in the *trans* isomer. It is possible to explain on this basis the slower rate of esterification of the second carboxyl in the *cis* form when compared to that in the *trans*. The three possible forms of these isomers are shown in Fig. 3.



Fig. 3.—Isomers of 1,2-cyclohexanedicarboxylic acid; the cyclohexane ring is perpendicular to the plane of the photograph: left, *cis* isomer; center, *trans* isomer showing tautomer with polar carboxyl groups; right, *trans* isomer showing tautomer with equatorial carboxyl groups. Photographs by Comer Shacklett.

For the 1,3-cyclohexanedicarboxylic acids, the

(12) Beckett, Pitzer and Spitzer, *ibid.*, **69**, 2488 (1947).

(13) See, for example, Rasmussen, *J. Chem. Phys.*, **11**, 249 (1943).

*trans* isomer has only one possible form and it has one polar and one equatorial acid group. The *cis* isomer has two possible tautomeric forms. Here one would probably expect the tautomer with the two equatorial carboxyls to predominate since in this form the acid groups are as widely separated as possible. Thus one would expect that the *cis* isomer by virtue of its two equatorial acid groups would have a  $k_1$  value about twice as great as that for the *trans* isomer. This is shown in Table IV. One would also expect the value of  $k_2$  to be greater for the *cis* than for the *trans* form. The three forms of the 1,3 acids are shown in Fig. 4.

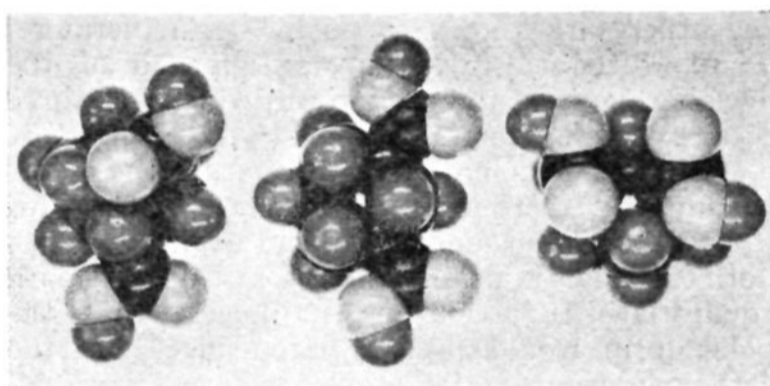


Fig. 4.—Isomers of 1,3-cyclohexanedicarboxylic acid; the cyclohexane ring is parallel to the plane of the photograph: left, *trans* isomer; center, *cis* isomer showing tautomer with equatorial carboxyl groups; right, *cis* isomer showing tautomer with polar carboxyl groups.

It is the *cis* form of 1,4-cyclohexanedicarboxylic acid which has only one tautomer, one acid group being polar and one equatorial. Of the two tautomeric forms of the *trans* isomer, it is again assumed that the form with two equatorial acid groups is predominant. If the equatorial acid group is more readily attacked, one would expect that the *trans* isomer would be esterified about twice as fast as the *cis*, and that the  $k_2$  value would also be greater for the *trans* form. This is shown in Table IV. Figure 5 illustrates the forms of the 1,4 isomers.

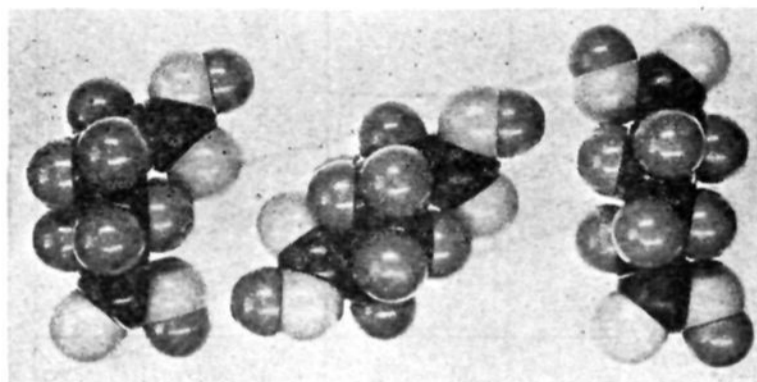


Fig. 5.—Isomers of 1,4-cyclohexanedicarboxylic acid; the cyclohexane ring is perpendicular to the plane of the photograph: left, *cis* isomer; center, *trans* isomer showing tautomer with polar carboxyl groups; right, *trans* isomer showing tautomer with equatorial carboxyl groups.

On this basis it is possible to explain the fact that the *cis*-1,3- and *trans*-1,4-cyclohexanedicarboxylic acids, each with two equatorial carboxyls, show almost identical behavior, while the *trans*-1,3 and *cis*-1,4 forms, each with one polar and one equatorial carboxyl, are similar to each other.

### Summary

The isomeric 1,2-, 1,3- and 1,4-cyclohexanedicarboxylic acids have been prepared in pure form, and their rates of acid-catalyzed esterification in methanol have been studied. Rate constants at four temperatures and activation energies have been tabulated.

It has been shown that the 1,3 and 1,4 isomers behave much like cyclohexanecarboxylic acid, but that the 1,2 isomers are esterified much more slowly.

The results are explained on the assumption that the cyclohexane ring is almost entirely in the chair form, and that whenever two tautomeric forms of the chair configuration are possible, the one yielding the greater separation of the substituents is predominant.

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