

## Salt Effects on the Racemization of Biphenyls

### I. The Racemization of 2,2'-Diiodo-4,4'-dicarboxybiphenyl Dianion in Aqueous Salt Solutions

PEDER BERNTSSON, MARIANNE WANGER and  
ROBERT E. CARTER

*Department of Organic Chemistry, University of Göteborg and Chalmers Institute of Technology, Gibraltargatan 5 A, Göteborg S, Sweden*

Salt effects on the rate of racemization,  $k$ , of 2,2'-diiodo-4,4'-dicarboxybiphenyl dianion in aqueous solutions have been investigated, and a linear relationship between  $\ln k$  and the ionic strength,  $J$ , was found up to  $J \approx 1.0$ , and no specific effects for different simple 1-1 salts were observed. This indicates, according to the theory of absolute reaction rates, that the salt effects are caused by differences in the activity coefficients for initial and transition states.

In agreement with previous observations, we have found a large dependence of  $\ln k$  on biphenyl concentration, which is probably caused by micelle formation.

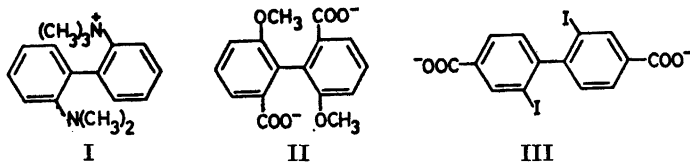
The greatest effect found by us was  $\ln(k/k_0) = 2.3 J$  for the case in which  $J$  was changed by varying the concentration of the Na-salt of 2,2'-diiodo-4,4'-dicarboxybiphenyl. These surprisingly large effects show that it is necessary to define the rate of racemization as the rate obtained by extrapolation of all salt concentrations to zero. This is also a thermodynamically well-defined rate constant, which should be used in the calculation of the activation parameters.

From the Kirkwood equation for the free energy change for a dipole caused by changes in the dielectric constant of the medium (which depends on  $J$ ), it is seen that the salt effects may be plausibly interpreted as being predominantly due to changes in the energy in the ground state instead of that of the transition state. Similar salt effects were previously explained by Lefler and Graham in terms of influences on the transition state.

The configurational inversion of optically active biphenyl derivatives has been widely investigated both experimentally<sup>1-4</sup> and theoretically.<sup>5,6</sup> The reaction is attractive from the experimental point of view due to its simple, first order kinetics and the accuracy with which the rate may be followed on an automatic reading polarimeter. Theoretically, the reaction has the advantage of having, at least in some cases,<sup>6</sup> a well-defined planar transition state

structure which has allowed the calculation of activation energies for several biphenyl derivatives<sup>5,6</sup> in fairly reasonable agreement with observed values.<sup>2,3,7</sup> The biphenyl derivatives which have been most profitably studied theoretically are those with halogen substituents in the 2- and 2'-positions, especially the dibromo and diiodo compounds.<sup>2,3,6</sup> The effect of 4,4'-substituents on the rate of racemization of the latter compound has been recently investigated by Chua Cheung King Ling and Harris,<sup>3</sup> who have discussed possible non-planar transition state conformations in some detail.

Salt effects on the rate of racemization of optically active biphenyls in aqueous solutions were first observed by Rieger and Westheimer<sup>7</sup> in their studies of 2,2'-diiodo- and 2,2',3,3'-tetraiodo-5,5'-dicarboxybiphenyl, and later extensively studied by Leffler and his co-workers,<sup>8,9</sup> who investigated biphenyls with charged groups in the 2- and 2'-positions. Rieger and Westheimer<sup>7</sup> found a linear correlation between the logarithm of the rate constant for the racemization and the ionic strength of the solution, but as these authors were primarily interested in the rate constant at zero ionic strength, obtained by extrapolation, they did not discuss the significance of salt effects *per se* in detail. Leffler and his co-workers<sup>8,9</sup> determined the rates of racemization



of the 2-(N,N,N-trimethyl)-2'-(N,N-dimethyl)-diaminobiphenyl cation (I) and the 2,2'-dimethoxy-6,6'-dicarboxybiphenyl dianion (II) in the presence of a large variety of salts. In the reaction of an optically active biphenyl with charged groups in the 2- and 2'-positions, both direct and indirect salt effects may come into play since the ions of the added salt can take part in specific interactions with the charged groups at the center of reaction as well as change the properties of the surrounding medium, making interpretations of these effects rather complicated.

We have chosen 2,2'-diiodo-4,4'-dicarboxybiphenyl dianion (III) for our studies of salt effects on biphenyl racemization because it is one of the simplest biphenyl derivatives whose water-soluble salts racemize at convenient rates at room temperature and above. Furthermore, in view of the absence of charged groups at the center of reaction, any observed influence of added inorganic salts on the rate constant may be rather safely attributed to indirect (medium) effects, and perhaps correlated with some parameter characteristic for the surrounding medium, such as the ionic strength.<sup>7</sup> This type of correlation may provide the basis for a better understanding of salt effects on organic reactions in general, as well as of the detailed mechanism<sup>3</sup> of the biphenyl inversion. Furthermore, such a correlation should afford a well-defined rate constant for use in the calculation of the activation parameters.<sup>7,10a</sup>

## THEORY OF SALT EFFECTS

Salt effects may be taken into account in the theory of absolute reaction rates by suitable modification of the expression<sup>10b</sup> for the observed rate constant  $k$  in a unimolecular reaction

$$k = \kappa \frac{kT}{h} K^\ddagger \quad (1)$$

In this expression, which refers to reactions in solution, all of the symbols have their usual significance, and we may replace  $K^\ddagger$ , the ratio of the concentration of molecules in the transition state to that of molecules in the initial state,

$$K^\ddagger = c^\ddagger/c \quad (2)$$

by  $K_0^\ddagger f/f^\ddagger$ , where  $K_0^\ddagger$  is the thermodynamic equilibrium constant for the equilibrium between the transition state and the initial state and the  $f$ 's are activity coefficients. Eqn. (1) may be written

$$k = \kappa \frac{kT}{h} K_0^\ddagger f/f^\ddagger = k_0 f/f^\ddagger \quad (3)$$

and  $k_0$  is the specific rate constant in an ideal solution. As noted by Glasstone, Laidler and Eyring,<sup>10a,b</sup>  $K_0^\ddagger$  is equal to  $\exp(-\Delta F^\ddagger/RT)$  where  $\Delta F^\ddagger$  is the sum of the standard free energy of activation due to *internal* factors only and the standard free energy of activation due to *solvation*. The activity coefficient ratio  $f/f^\ddagger$  is equal to  $\exp(-\Delta F_{\text{salt}}^\ddagger/RT)$  due to the non-ideality caused by the presence of salts in the aqueous medium in which the reaction occurs.

To obtain the free energy of activation due to *internal* factors it would be necessary to measure the rate of reaction in the gas phase. The magnitude of the free energy of activation due to solvation has been discussed by Cagle and Eyring<sup>11</sup> for the case of biphenyl racemization.

In aqueous solutions activity coefficients may be expressed in terms of the ionic strength  $J$  in the following way

$$\begin{aligned} \ln f &= -A \sqrt{J} + BJ \\ \ln f^\ddagger &= -A^\ddagger \sqrt{J} + B^\ddagger J \end{aligned} \quad (4)$$

$A$  is a constant for a given solution, the numerical value of which depends upon the ionic charge of the solute, the dielectric constant of the solvent, the ionic strength and the parameter  $\bar{a}$ , defined as the mean distance of approach of the positive and negative ions.<sup>12</sup> None of these factors is expected to change significantly between the initial and transition states in the inversion of a 2,2'-dihalobiphenyl, and thus we assume  $A^\ddagger = A$ . The  $B$ -terms in eqn. (4) represent the effect of the dissolved ions on the dielectric constant of the medium, and this effect is assumed to vary linearly with the ionic strength.<sup>12</sup> If the solution contains large organic ions, not only the influence of charged groups on the orientation of surrounding water molecules, but also the orienting effect of possible dipoles in the organic molecule must be taken into account

in the  $B$ -term. In view of the fact that the initial state in the inversion of a 2,2'-dihalobiphenyl is expected to be more polar than the transition state, it is to be expected that  $B \neq B^\ddagger$ . The biphenyl goes from an initial state "cis"-halogen configuration<sup>14</sup> to a more or less planar "trans" configuration in the transition state. If eqn. (3) is written in logarithmic form and then combined with eqn. (14), assuming  $A = A^\ddagger$ , the expression

$$\ln k = \ln k_0 + (B - B^\ddagger)J \quad (5)$$

is obtained. This is the equation used by Brönsted<sup>13</sup> for the reaction between an ion and an uncharged molecule. According to eqn. (5), a plot of  $\ln k$  vs.  $J$  should give a straight line with slope  $(B - B^\ddagger)$ . Furthermore, the slope should be independent of the nature of the added salt if the salt is a strong electrolyte because both  $B$  and  $B^\ddagger$  depend only upon the nature of the reacting molecule and its immediate environment. A linear relation between  $\ln k$  and  $J$  (which by convention depends only upon the concentration of added salt and the charge of the formed ions) involves the tacit assumption that the solvation of the reacting organic molecule is not influenced by the presence of inorganic ions in the solution. The formation of micelles due to poor solvation of the hydrocarbon portion of a large organic ion may conceivably lead to preferential reaction within the micelles, and thus in a medium in which the magnitude of the factor  $B - B^\ddagger$  is different from that obtained in a purely aqueous environment. A plot of  $\ln k$  vs.  $J$  is expected<sup>8</sup> to give a straight line even in this case, but the slope may vary with the nature of the added salt since the degree of micelle formation should be influenced by the capacity of the added ions for binding water molecules. The salt of an optically active biphenyl may itself be considered an "added salt" and, on the basis of the above line of reasoning, the rate of racemization is expected to be concentration-dependent, as observed by Rieger and Westheimer,<sup>7</sup> Leffler and co-workers<sup>8,9</sup> and in the present work (*vide infra*).

From the intercept of a plot of  $\ln k$  vs.  $J$  the rate constant for the racemization at zero ionic strength ( $k_0$ ) may be obtained. This rate constant is characteristic for the reaction since it refers to a thermodynamically well-defined ideal state, the infinitely dilute solution. Thus, as pointed out by Rieger and Westheimer,<sup>7</sup>  $k_0$  and not  $k$ , the rate constant measured at a more or less arbitrary ionic strength, should in principle be used in the determination of activation parameters.

## RESULTS

The rate of racemization of the 2,2'-diiodo-4,4'-dicarboxybiphenyl dianion (III) in aqueous solutions containing different salts at various concentrations was determined at  $25.0 \pm 0.1^\circ\text{C}$ . The ionic strength of the solutions varied from 0.06 to 1.7. In the calculation of the ionic strength, the biphenyl dianion may be included either *i*) as an ordinary divalent ion or *ii*) as two independent negatively charged ions. The Debye-Hückel theory of ionic strength is actually valid for small inorganic ions which may be approximated as charged spheres, and it is thus not obvious which of the above alternatives is most correct. The contribution of the biphenyl dianion and its accompanying metal ions

to the ionic strength is 0.12 according to *i*) and 0.08 according to *ii*). We have somewhat arbitrarily chosen alternative *i*), but it may easily be shown that, within our limits of error, this choice affects none of the results discussed here, nor does it influence our conclusions.

In Fig. 1  $\ln k$  is plotted *vs.*  $J$  where  $J$  was changed by varying the concentration of added inorganic salt and maintaining the biphenyl concentra-

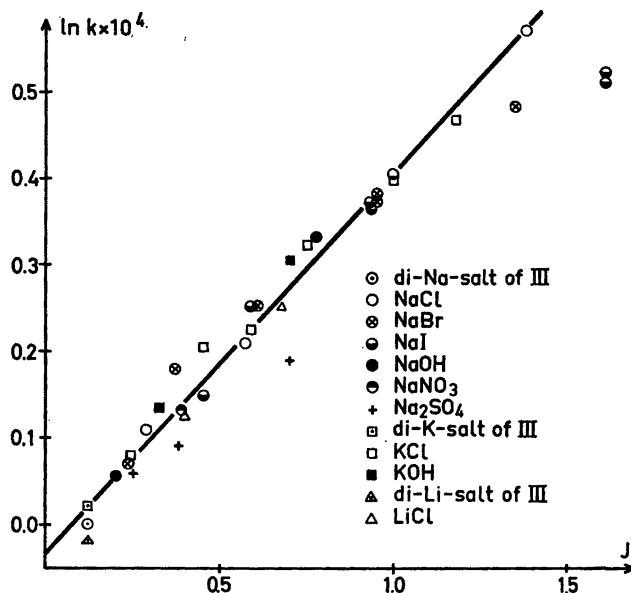


Fig. 1. Plot of  $\ln k \times 10^4$  *vs.*  $J$  at 25.0°C for the racemization of III in aqueous solutions containing inorganic salts.

tion constant at 0.020 g/ml solvent. The plot gives a reasonably good straight line with a slope independent of the nature of the added salt up to  $J \approx 1$  for uni-univalent salts and up to  $J \approx 0.5$  for a uni-divalent salt. Thus, in dilute solutions agreement with eqn. (5) is acceptable, and the salt effects of small ions may be interpreted in terms of a difference in activity coefficients for initial and transition states in the inversion of the biphenyl dianion. This difference in activity may be primarily attributed to the difference in polarity between the initial and transition states. The slope of the plot in Fig. 1, ( $B - B^\ddagger$ ), was calculated to be 0.44 by a least-squares treatment of the data.

In Fig. 2  $\ln k$  is plotted *vs.*  $J$  where  $J$  was changed by varying the biphenyl concentration. The plot gives a straight line, in agreement with the results of Rieger and Westheimer.<sup>7</sup> From Fig. 2 the value  $k_0 = 0.75 \times 10^{-4} \text{ sec}^{-1}$  is obtained by extrapolation to zero ionic strength. This value is the rate constant characteristic for the racemization of 2,2'-diiodo-4,4'-dicarboxybiphenyl dianion in infinitely dilute aqueous solution at 25.0°C. The rates of racemization obtained by Chua Cheung King Ling and Harris<sup>3</sup> at 30.3°C and 55.0°C

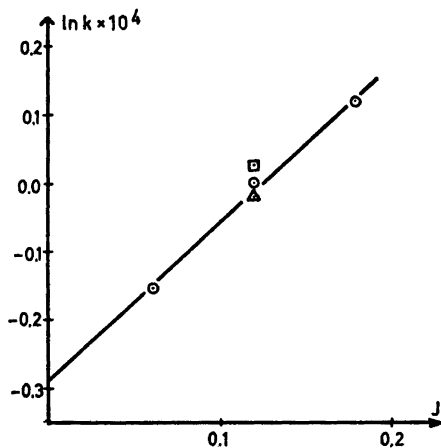


Fig. 2. Plot of  $\ln k \times 10^4$  vs.  $J$  at 25.0°C for the racemization of III in aqueous solutions. For symbols see Fig. 1.

( $1.44 \times 10^{-4} \text{ sec}^{-1}$  and  $2.20 \times 10^{-3} \text{ sec}^{-1}$ , resp.) correspond very well with those obtained by us at the same temperatures ( $1.49 \times 10^{-4} \text{ sec}^{-1}$  and  $2.28 \times 10^{-3} \text{ sec}^{-1}$ ) if we reproduce their concentrations (at 30.3°C: 0.0070 g of 2,2'-diiodo-4,4'-dicarboxybiphenyl/ml 0.1 N NaOH and at 55.0°C: 0.0078 g/ml 0.1 N NaOH).\*

#### DISCUSSION

The racemization of (I) has been carefully investigated by Graham and Leffler<sup>8</sup> in the presence of a large number of salts at two different temperatures. They demonstrate the existence of an isokinetic relationship which, as the authors point out,<sup>8</sup> may nonetheless be devoid of significance in view of the small changes in  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ . Wiberg<sup>15</sup> has shown that in such cases the error in  $\Delta H^\ddagger$  is directly proportional to the error in  $\Delta S^\ddagger$ , and a linear relation between  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  is always observed in these cases. Leffler and Graham<sup>8</sup> separate the observed salt effects into two classes: *i*) the effects of small ions and *ii*) the effects of large organic ions. The authors conclude that the effects of small ions may be attributed to their capacity for binding water molecules and thus assisting in the promotion of the biphenyl to the transition state, which is thought to be accompanied by the release of water molecules from the solvation shell of (I) to the solution in general. Application of eqn. (5) to the data of Leffler and Graham<sup>8</sup> on the effects of added salts at 79.4°C and 100°C leads to the plots shown in Fig. 3.

The slopes of the lines in Fig. 3 give  $(B - B^\ddagger) \approx 0.0$  in both cases. This value is small compared with that obtained in the present investigation (0.44). It has been suggested<sup>12</sup> that the  $B$ -term in the equation for the activity coefficient (4) expresses the effect of the dissolved ions on the dielectric constant ( $D$ ) of the solution.

\* Private communication from M. M. Harris.

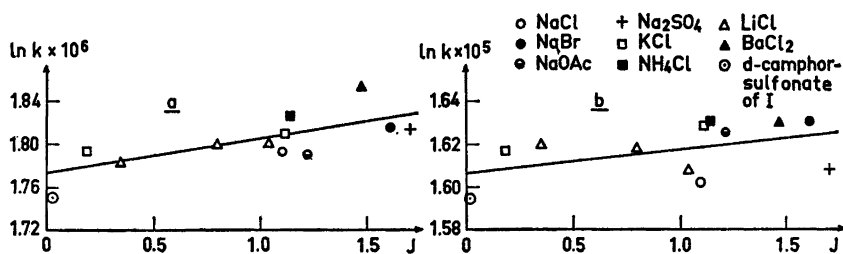


Fig. 3a. Plot of  $\ln k \times 10^6$  vs.  $J$  at  $79.4^\circ\text{C}$  for the racemization of I in aqueous salt solutions. The values have been taken from Ref. 8. For symbols see Fig. 3.b

Fig. 3b. Plot of  $\ln k \times 10^5$  vs.  $J$  at  $100^\circ\text{C}$  for the racemization of I in aqueous salt solutions. The values have been taken from Ref. 8.

The ions of the added salts presumably do not directly participate in the inversion reaction, nor do they show any individual effects at ionic strength less than 1.0. It may therefore be safely assumed that the only effect which must be considered in dilute solutions is that on the dielectric constant of the medium. The presence of ions in a solution is expected to decrease  $D$  as a result of the orienting effect of ionic charge on nearby dipoles.\* The measurements reported in the present work indicate that the term  $f/f^\ddagger$  in eqn. (3) increases as the ionic strength  $J$  increases. As previously noted,<sup>10a,b</sup> this term equals  $\exp(-\Delta F_{\text{salt}}^\ddagger/RT)$ , *i.e.* that part of the energy of activation which depends on external factors such as the presence of ions in the surrounding medium. This relation implies that  $\Delta F_{\text{salt}}^\ddagger$  decreases as  $J$  increases, *i.e.* as  $D$  decreases.

According to the theory of Kirkwood,<sup>16</sup> the free energy change involved in the transfer of a dipole from vacuum to a medium of dielectric constant  $D$  is given by

$$\delta F = -\mu^2/r^3 (D - 1)/(2D + 1) \quad (6)$$

where  $\mu$  is the dipole moment and  $r$  the molecular radius. For a biphenyl molecule undergoing inversion, the radii of the initial and transition states may be assumed to be approximately equal. The validity of this assumption is supported by the work of McCune *et al.*<sup>17</sup> who investigated the pressure dependence of the rate of racemization of (-)-6-nitro-2,2'-dicarboxybiphenyl in 0.1 N NaOH. From this work it may be estimated that the difference in molecular volume between initial and transition states,  $\Delta V^\ddagger$ , is less than 1.6 ml/mole at 1 atm and  $52^\circ\text{C}$ , which is quite small compared with the total molecular volume of 233 ml/mole. Volume changes of activation of the same order of magnitude have been determined by McKelvey and Brower<sup>18</sup> for the racemization of other compounds in which optical activity is due to hindered rotation about a single bond. These data also indicate that the difference in solvation between initial and transition states is not pronounced, in contrast to the suggestion of Graham and Leffler.<sup>8</sup>

\* The reaction takes place in a strongly polar medium where "short-range effects" such as van der Waals forces between the biphenyl and the solvent may be neglected compared with dipole-dipole interactions.

The near absence of changes in solvation between initial and transition states indicates that the difference in free energy due to medium effects,  $\Delta F_{\text{salt}}^\ddagger$ , depends only upon solute-medium interactions of dipolar character.

If  $\mu^\ddagger$  is the dipole moment of the transition state and  $\mu$  is the dipole moment of the initial state, eqn. (6) can be used to calculate the difference in free energy between the two states caused by this effect. The following expression is obtained

$$\Delta F_{\text{salt}}^\ddagger = -(D - 1)/(2D + 1) 1/r^3 (\mu^{\ddagger 2} - \mu^2) \quad (7)$$

The function  $(D - 1)/(2D + 1)$  is an increasing function of  $D$ , and thus the term  $(\mu^{\ddagger 2} - \mu^2)$  must be negative if  $\Delta F_{\text{salt}}^\ddagger$  is to decrease as  $D$  decreases, as indicated by our measurements on (+)-2,2'-diiodo-4,4'-dicarboxybiphenyl dianion. This implies that  $\mu > \mu^\ddagger$ , in agreement with our assumption (*vide supra*) about the expected change in dipole moment on going from the initial state "cis"-halogen configuration<sup>14</sup> to the more or less planar "trans" configuration of the transition state. This leads to a decrease in the energy gap between the two states as  $D$  decreases. From this difference in polarity between the initial and transition states, it is seen from eqn. (6) that the effect of added salt upon the racemization may be plausibly interpreted as being predominantly due to an increase in the free energy in the initial state instead of a decrease of the free energy in the transition state.<sup>8</sup>

The smaller  $B - B^\ddagger$  values obtained for the cation (I) may be analogously interpreted in terms of a smaller change in polarity on going from the initial state to the transition state.

From the work of Graham and Leffler<sup>8</sup> it is evident that the rate of racemization increases linearly with the concentration of large organic ions and that the effect is specific for each such added ion and different from that caused by small ions. This difference may be seen by comparing Figs. 3b and 4. Fig. 3b shows the effect of added salt at 100°C and constant concentration of (I) (0.02 M), while Fig. 4 shows the effect of organic ions, *i.e.* the biphenyl

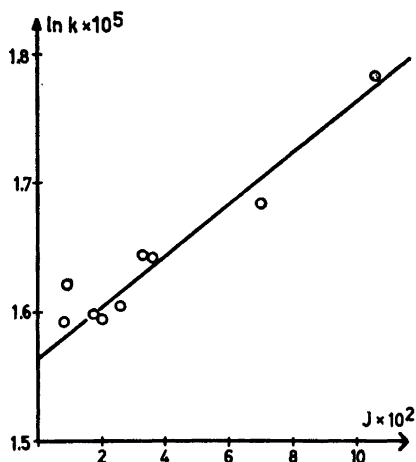


Fig. 4. Plot of  $\ln k \times 10^5$  vs.  $J$  at 100°C for the racemization of the *d*-camphor-sulfonate of I in aqueous solutions. The values have been taken from Ref. 8.



(I) itself, at the same temperature. From Fig. 4,  $k_0$  has been determined to be  $4.77 \times 10^{-5} \text{ sec}^{-1}$  at  $100^\circ\text{C}$ .

### CONCLUSIONS

The present study indicates that the investigation of salt effects on biphenyl racemization can yield information about the difference in polarity between initial and transition states, provided that the molecule lacks charged groups in the 2 and 2' positions. The effect of small ions appears to be interpretable as a long-range effect due to a change in the dielectric constant of the medium. We favor this interpretation instead of that offered by Graham and Leffler,<sup>8</sup> who postulated a change in solvation between initial and transition states.

It is evident from the results of the present investigation that the rate of racemization of a biphenyl in aqueous solution may be conveniently defined as that obtained by extrapolation of all salt concentrations to zero (*i.e.*, extrapolation to zero ionic strength). It is such extrapolated rate constants which should be used in the calculation of the activation parameters, as pointed out by Rieger and Westheimer,<sup>7</sup> since they refer to a thermodynamically well-defined ground state.

### EXPERIMENTAL

Optically active 2,2'-diiodo-4,4'-dicarboxybiphenyl was synthesized as described by Chua Cheung King Ling and Harris<sup>3</sup> except for a procedural modification in the preparation of the intermediate methyl-3-nitro-4-iodobenzoate.<sup>3</sup> We obtained (+)-2,2'-diiodo-4,4'-dicarboxybiphenyl as the result of secondary asymmetric transformation with brucine, whereas the previous workers<sup>3</sup> obtained the (-) isomer by the same procedure.

The test solutions were prepared by adding two equivalents of a base ( $a$  ml of aqueous NaOH, KOH or LiOH) to 0.100 g of (+)-2,2'-diiodo-4,4'-dicarboxybiphenyl. Thereupon 5.0 -  $a$  ml of a Na, K, or Li salt solution of known concentration was added. Only salts of the alkali metals could be used because otherwise a precipitate was obtained in the test solution.

The salt concentration of the test solutions was calculated and its molality,  $m$ , was obtained from

$$m = c/\rho$$

where  $\rho$  is the density of the added salt solution neglecting the biphenyl concentration (0.04 M).  $\rho$  was obtained from *Handbook of Chemistry and Physics*, 45th Ed. (1965), except for NaI where  $\rho$  was measured with a densimeter.

All salts were *pro analysi* grade, and the water had been deionised by passage through a "Quickpure professional model" ion exchanger.

The decrease in optical activity was followed on a Perkin-Elmer 141 polarimeter. The deviation in each reading is assumed to be  $\pm 0.002^\circ$ . The test solution was contained in a 10 cm jacketed tube maintained at  $25.0 \pm 0.1^\circ\text{C}$  by circulating water from a thermostat. Each reaction was followed for about one half-life, and 10 to 15 readings were made during each run. In control runs in which the reaction was followed for at least 10 half-lives, no drift in the first order rate constant was observed.

The racemization of a biphenyl is a first order reaction and the rate constant for the racemization may be calculated from the equation

$$\ln \phi = -kt + \text{const.}$$

where  $\phi$  is the measured optical rotation at time  $t$ . It should be borne in mind that the rate of *inversion* is half of the rate of racemization.

The rate constant  $k$  and the standard error were calculated by a least-squares treatment of the kinetic data. The standard error was about 0.3 % of the rate constant at the lowest ionic strengths.

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