D_2O, as seen in Table IV. The small difference observed may be ascribed to a solvent effect between H_2O and D_2O.

In the case of diethylphosphonate k_{AcOH} for the exchange reaction was estimated to be $\sim 6 \times 10^{-3}$ M^{-1} min.$^{-1}$, as compared to a value of 0.3×10^{-3} M^{-1} min.$^{-1}$ obtained by Nylen[2] for the oxidation reaction. No explanation is offered for this difference.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, VANDERBILT UNIVERSITY, NASHVILLE 5, TENNESSEE]

The Hydrolysis of the *d*- and *l*-Forms of $H[As(C_6H_4O_2)_3 \cdot H_2O]$ in the Presence of Added Asymmetric Species

BY JOHN H. CRADDOCK AND MARK M. JONES[1]

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An examination of the rates of hydrolysis of the *d* and the *l* forms of $H[As(C_6H_4O_2)_3 \cdot H_2O]$ in the presence of varying concentrations of several added asymmetric species resulted in no differences between enantiomers greater than the estimated experimental error of about 2%. These results indicate that configurational activity effects involving electrolytes in homogeneous solution may be very small in some systems. A discussion of previously reported cases shows that several related aspects of the behavior of solutions in which such phenomena have been reported are only imperfectly known. The problem of the quantitative estimation of configurational activity effects cannot be solved until these related problems are solved.

In 1951, Dwyer, Gyarfas and O'Dwyer[2,3] reported several lines of evidence that indicated the activities of enantiomeric species, in homogeneous solution, were affected differently upon the addition of a third optically active species. While this type of difference must ultimately be the basis for the formation of diastereoisomers, these had not previously been delineated clearly in homogeneous solution. One of the most interesting aspects of this is the "configurational activity" effect on the rates of racemization of the *d* and *l* forms of [Ni(*ortho*-phenanthroline)$_3$]$^{+2}$ (hereafter abbreviated Ni(phen)$_3^{+2}$). This results in rates for the *d* and *l* forms which differ by as much as 15% in the presence of an added optically active electrolyte.[4] The present study was undertaken to delineate the kinetic aspects of configurational activity in greater detail and to establish the nature of the variables governing its magnitude. It was hoped that a quantitative basis for prediction of the magnitude of such effects might be developed.

The system chosen for this work was the arsenic(V)-catechol complex, $H[As(C_6H_4O_2)_3 \cdot H_2O]$, whose general kinetic behavior was established in an earlier study.[5] This system was considered ideal because firstly, the two enantiomorphic forms can be obtained easily in a state of high optical purity and secondly, these forms are known to undergo a second order asymmetric transformation very readily in the presence of suitable optically active bases such as quinine, cinchonine, cinchonidine and quinidine.[6,7] A review of the entire group of phenomena reported as "configurational activity" has been given by Basolo and Pearson.[8] The present work is concerned *only* with the kinetic aspects of this phenomenon in *homogeneous solutions of electrolytes*.

Experimental

Apparatus.—A Rudolph Model 62 polarimeter, reading to 0.05°, was used in the kinetic studies on the arsenic complexes. A 4 dm. jacketed polarimeter cell held the sample while water maintained to within ±0.02° of the reported temperature by a thermoregulator, was circulated through its jacket. A Schmidt and Haensch polarimeter reading to 0.01° was used in the kinetic studies on the nickel complexes together with a 2 dm. jacketed cell whose temperature was similarly regulated.

Materials.—The resolution of the arsenic complexes was effected by the procedure of Mann and Watson.[7] The molecular rotations of the complexes used were: $Ba[As(C_6H_4O_2)_3 \cdot H_2O]_2$, *d* form, $[\alpha]^{25}\text{D}$ +416°; *l* form, $[\alpha]^{25}\text{D}$ −416. The literature values are for the *d* form,[6] $[\alpha]^{25}\text{D}$ 418.7°; *l* form, $[\alpha]^{25}\text{D}$ −417.5°[6]; −438°.[7] The nickel orthophenanthroline complexes were prepared and resolved using the method given by Dwyer and Gyarfas.[9]

The specific rotations were obtained after storage for ten days in a refrigerator and were: *d* perchlorate, $[\alpha]^{20}\text{D}$ 1381°; literature[9] $[\alpha]^{20}\text{D}$ 1463°; *l* perchlorate, $[\alpha]^{20}\text{D}$ −1390°; literature[9], $[\alpha]^{20}\text{D}$ −1463°. The purity of the samples that were used was thus only 97%, but this seemed to be not detrimental to the reproducibility of the rates.

The buffered solutions were prepared on the basis of the solutions described by Clark and Lubs[10] but also contained added optically active electrolytes. The compositions of these solutions are given in Table I. They were used as solvent solutions in the kinetic runs; the appropriate amount of optically active barium salt was weighed up and dissolved in the buffer solution and then the rate of loss of optical activity was determined for the resulting solution. The amino acids used were "Standardized Amino Acids" obtained from the Nutritional Biochemicals Corp. The ammonium salt of *d*-α-bromocamphor-π-sulfonic acid (abbreviated BCS in the Tables) was obtained from the Aldrich Chemical Co., Milwaukee, Wis. It was found necessary to purify the salt to remove water soluble colored im-

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[1] To whom correspondence concerning this paper should be sent.

[2] F. P. Dwyer, E. G. Gyarfas and M. F. O'Dwyer, *Nature*, **167**, 1036 (1951).

[3] F. P. Dwyer and E. C. Gyarfas, *ibid.*, **168**, 29 (1951).

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[6] A. Rosenheim and W. Plato, *Ber.*, **58**, 2000 (1925).

[7] F. G. Mann and J. Watson, *J. Chem. Soc.*, 505 (1947).

[8] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, pages 283–289.

[9] F. P. Dwyer and E. C. Gyarfas, *J. Proc. Roy. Soc.*, *New South Wales*, **83**, 232 (1949).

[10] I. M. Kolthoff and H. A. Laitinen, "*p*H and Electro Titrations," John Wiley and Sons, Inc., New York, N. Y., 1940, pages 32–35.

TABLE I

COMPOSITION OF STOCK SOLUTIONS CONTAINING OPTICALLY-ACTIVE ELECTROLYTES[a]

	Solution	Added elect., g.	0.2 N HCl, ml.	0.2 N KCl, ml.	pH		Concn. HCl,[d] ml.
					Clark and Lubs	Obsd.	
A	2% BCS[b]	2.00	5.30	25.0[c]	2.0	1.4	
B	4% BCS	4.00	5.30	25.0	2.0	2.0	
C	6% BCS	6.00	5.30	25.0	2.0	2.0	
D	10% BCS	10.00	5.30	25.0	2.0	2.0	
E	1% L-Aspartic acid	1.00	3.35	25.0	2.2	1.55	0.63
F	3% L-Aspartic acid	3.00	5.30	25.0	2.0	1.22	1.86
G	5% L-Aspartic acid	5.00	5.30	25.0	2.0	1.20	1.11
H	1% L-Lysine·2 HCl	1.00	3.35	25.0	2.2	1.67	
I	4% L-Lysine·2 HCl	4.00	3.35	25.0	2.2	1.33	
J	10% L-Lysine·2 HCl	10.00	3.35	25.0	2.2	1.08	
K	1% L-Glutamic acid·HCl	1.00	3.35	25.0	2.2	1.60	
L	5% L-Glutamic acid·HCl	5.00	3.35	25.0	2.2	1.22	
M	10% L-Glutamic acid·HCl	10.00	3.35	25.0	2.2	1.00	
N	1% L-Cysteine·HCl·H_2O	1.00	3.35	25.0	2.2	1.50	
O	5% L-Cysteine·HCl·H_2O	5.00	3.35	25.0	2.2	1.10	
P	10% L-Cysteine·HCl·H_2O	10.00	3.35	25.0	2.2	0.90	

[a] All values based on total volume of 100 ml. [b] $NaClO_4$ added to maintain constant ionic strength ($\mu = 3.0$), BCS = ammonium *d*-bromocamphor-π-sulfonate. [c] NaCl used in place of KCl. [d] 37–38% HCl, sp. gr. 1.19.

purities. As it proved impossible to obtain a convenient purification procedure from the literature, a simple one was developed. This involved passing a hot aqueous solution of the ammonium salt through an alumina column prepared by packing Merck Reagent Grade Aluminum oxide in a glass tube. The desired ammonium salt was readily eluted as a colorless solution by hot water; the colored impurity remained on the column. This salt was then recrystallized from water, dried over anhydrous calcium chloride and stored until ready for use. A 2% aqueous solution of the recrystallized ammonium salt had $[\alpha]^{25}\text{D}$ 84.4°. The literature value[11] is $[\alpha]^{9}\text{D}$ 84.8°.

Procedure.—The procedure used in a typical kinetic run was as follows: A solid sample of the optically active salt was weighed out on an analytical balance and transferred quantitatively to a dry volumetric flask. Generally, the weight of solid salt was such that solutions of the barium salt were obtained with concentrations in the range 2.25×10^{-3} M to 5.0×10^{-3} M. All washings and rinsings necessary in the transfer were accomplished using the appropriate buffer solution in which the salt was to be dissolved. Then the solution in the flask was diluted to volume using the same buffer solution, shaken for three minutes and filtered, using suction, to remove any undissolved solid that remained. This filtration was necessary to insure an absolutely clear solution. The polarimeter cell then was rinsed several times with the filtered solution, filled and stoppered. Finally, the jacketed cell was placed in the polarimeter and connected to the circulating pump of the constant temperature bath. The cell and its contents now were allowed to come to the temperature of the bath. This usually required only a few minutes since the buffered solutions were themselves equilibrated to the bath temperature before the beginning of the run. After equilibration to the bath temperature, measurements of optical rotation (α) were obtained as a function of time (t). The entire sequence of manipulations from the time of mixing to the first measurement was carried out in less than ten minutes. When the Rudolph polarimeter was used, as many measurements, generally five or six, were made in a time 30 seconds prior to the time t as could be accomplished by approaching the equal intensity field from alternate sides. The rates of racemization of the nickel (II) complexes were much slower so the initial mixing time was a very small proportion of the total time of the run ($\sim$ 18 hr.).

Results and Discussion

The results of the studies on the arsenic(V) complex are presented in Table II. The k's are all first order rate constants. These data show that, within the limits of our experimental error, there is no obvious evidence for a configurational activity effect. This wholly unexpected result raised a number of questions, the most important of which concerned the magnitude of the result in the original studies on the nickel(II) complexes. Some of these were accordingly repeated. These results are shown in Table III along with the corresponding data of Davies and Dwyer.[4]

An analysis of the percentage uncertainty in the rate constants of the studies reporting this effect can be carried out using equations presented by Benson.[12] An early report of the differing rates in the hydrolysis of tris-(biguanide)-cobalt(III)-chloride-*d* tartrate was carried out with temperature control of ±1°.[13] This can be shown to result in an uncertainty in the rate constants of ±10% for a reaction with an activation energy in the range reported, *i.e.*, 22,310 cal. for the *l* form. The variations in the rate constants which were considered to represent significant differences ranged from 5% to 0.5%. In the work of Davies and Dwyer it is not possible to make an estimate of their percentage uncertainty from the published data, but it seems reasonable to assume their uncertainty to be no greater than ours and possibly less. One may then look for differences in the types of system studied for an explanation. It should be mentioned that Davies and Dwyer stated that studies showing that first order asymmetric transformations do not occur in non-aqueous solvents would be published in a subsequent paper. Although a paper on the racemization of Ni(phen)$_3^{+2}$ in non-aqueous solvents was published,[14] it does not mention such studies.

If one considers only the results on the arsenic(V) complex one is forced to the conclusion that any possible effect is smaller than the natural variations set by the limits of control over the environment of the reacting system. Since this effect would be

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(11) I. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Vol. I, Eyre & Spottiswoode, London, 1953, 314.

(12) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pages 86–94.

(13) P. Ray and N. K. Dutt, *J. Indian Chem. Soc.*, **20**, 81 (1943).

(14) N. R. Davies and F. P. Dwyer, *Trans. Faraday Soc.*, **50**, 1325 (1954).

TABLE II

SUMMARY OF RESULTS FOR THE HYDROLYSIS OF *d*- AND *l*-Ba[As$(C_6H_4O_2)_3 \cdot H_2O]_2$ IN THE PRESENCE OF OPTICALLY ACTIVE ELECTROLYTES

	Solution	Temp., °C.	*p*H (Clark and Lubs)	$k_d \times 10^3$ min.$^{-1}$	$k_l \times 10^3$ min.$^{-1}$
A	2% Ammonium *d*-α-bromo-camphor-π-sulfonate	25	2.0	22.0 21.5	21.2 21.3 21.5
A	2% Ammonium *d*-α-bromo-camphor-π-sulfonate	20	2.0	11.1 11.2	11.1
B	4% Ammonium *d*-α-bromo-camphor-π-sulfonate	25	2.0	4.12	4.08
C	6% Ammonium *d*-α-bromo-camphor-π-sulfonate	30	2.0	9.06	8.94
D	10% Ammonium *d*-α-bromo-camphor-π-sulfonate	30	2.0	9.93	9.94
E	1% L-Aspartic acid	25	2.2	11.9	11.9
F	3% L-Aspartic acid	30	2.0	42.0	42.3
G	5% L-Aspartic acid	30	2.0	42.5	42.8
H	1% L-Lysine dihydrochloride	25	2.2	7.15	7.14
I	4% L-Lysine dihydrochloride	25	2.2	11.2	11.2
J	10% L-Lysine dihydrochloride	25	2.2	14.0	14.1
K	1% L-Glutamic acid hydrochloride	25	2.2	9.11	9.11
L	5% L-Glutamic acid hydrochloride	25	2.2	18.5	18.5
M	10% L-Glutamic acid hydrochloride	25	2.2	25.7	25.8
N	1% L-Cysteine hydrochloride	25	2.2	12.7	12.7
O	5% L-Cysteine hydrochloride	25	2.2	22.1	22.4
P	10% L-Cysteiene hydrochloride	25	2.2	28.8	28.6

TABLE III

RATES OF RACEMIZATION OF *d*- AND *l*-[Ni(*o*-phen)$_3$]$^{+2}$ IN THE PRESENCE OF INERT OPTICALLY ACTIVE ELECTROLYTES

Solution	Temp., °C.	$kd \times 10^4$, min.$^{-1}$	$kl \times 10^4$, min.$^{-1}$	kd/kl	Sources
4% Ammonium *d*-α-bromocamphor-π-sulfonate	24.85	1.53	1.71	0.895	4
5% Ammonium *d*-camphorsulfonate	25.0	2.03	2.15	0.945	4
4% Ammonium *d*-α-bromocamphor-π-sulfonate	25.0	1.52	1.50	1.01	This work
4% Ammonium *d*-α-bromocamphor-π-sulfonate	25.0	1.58	1.46	1.08	This work

exerted through a slight variation in the activity coefficients and hence the concentrations of activated complexes concerned, the usual rules governing interactions responsible for changes in activity coefficients, might be expected to apply here. If the arsenic complex were only slightly ionized the interaction with added ionic species might be expected to be relatively small. Under such conditions the possibility of large configurational activity effects may be restricted to those systems in which a second phase appears.[3] It is of interest to note that in organic systems such effects are shown by salts only in solvents "in which ionic dissociation is largely absent."[15] One would also expect less ion pair formation between the singly charged complex arsenic(V) ion and other ions than between the doubly charged nickel(II) complex ions studied by Davies and Dwyer. The objection that one would not expect any effect of one anion (cation) on another anion (cation)[15] is difficult to interpret in view of the report[4] that the change produced in the ratio k_d/k_l for Ni(phen)$_3^{+2}$ by 2% *d*-cinchoninium sulfate is roughly equal in magnitude (but opposite in sign) to that produced by a 4% solution of ammonium *d*-bromcamphorsulfonate. This and related observations in the literature (collected in reference 15) violate the Brønsted principle of specific interaction which leads to the expectation that any such configurational activity effects on activity coefficients would be greatest between ions of opposite charge.

Some of the other evidence for configurational activity in homogeneous solution consists of the frequently reported changes in optical rotatory power obtained with mixtures consisting of a pair of enantiomorphs and an added optically active material.[8,15] This phenomenon is certainly well established, but its claim for attention is considerably reduced when it is noted that mixtures of optically active materials do not necessarily show an additive rotatory power.[16]

Superimposed on these effects are the accompanying changes in both rates and rotations produced by very large ions. These changes are of the same order of magnitude as the change produced by any configurational activity effects. Unfortunately the experimental evidence on these related problems is very sparse.[17]

In conclusion it seems reasonable to expect that configurational activity effects with *ionized com-*

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(15) E. E. Turner and M. M. Harris, *Quart. Revs.*, 1, 300 (1948).

(16) J. R. Partington, "An Advanced Treatise on Physical Chemistry," Vol. IV, Longmans, Green and Co., London, 1953, pages 340–346, 365 ff. contains a discussion of this. Most of the older examples from the literature are collected in H. Landolt "Optical Rotatory Power," Chemical Publishing Co., Easton, Pa., 1902. G. Kortum, "Das optische Verhalten geloster Electrolyte," F. Enke, Stuttgart, 1936, p. 86, discusses some very carefully studied examples.

(17) The referee has called attention to the fact that the phenomenon considered here is closely related to the Pfeiffer Effect. This has been studied by R. C. Brasted, Ph.D. Thesis, University of Illinois, 1942, and Brasted's work is also discussed, along with related material in (a) J. C. Bailar, Jr., "The Chemistry of the Coördination Compounds," Reinhold Publishing Co., New York, N. Y., 1956, pages 581–583. (b) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., London, 1958, pages 285–289.

plex salts in homogeneous single phase systems will be of much smaller magnitude than those found for two phase systems. It would be hoped that studies of such effects would be accompanied by concurrent examination of the precision of the measurements, the effect of the size of the added electrolyte and an examination of the systems over a range of concentrations of the added asymmetric electrolyte.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY, STANFORD, CALIFORNIA]

Spectrophotometric Study of a Thiocyanate Complex of Iodine[1,2]

BY CARL LEWIS AND D. A. SKOOG

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Iodine and thiocyanic acid were found to give a 1:1 complex in both aqueous and ether solutions which absorbs strongly in the ultraviolet region. In ether, 2 moles of water are consumed in forming the complex. The thermodynamic properties of the species have been determined in aqueous solution over a temperature range of 7.6 to 16.5°. The formation constant at 25° in solution of ionic strengths of 1 to 5 is estimated to be 85; the ΔH^0 for the reaction is -8.1 kcal./mole.

There is a good deal of indirect evidence for the existence in aqueous solution of one or more iodine–thiocyanate complexes. For example, it is found that rather large quantities of iodine will dissolve rapidly in aqueous potassium thiocyanate to give solutions which are yellow or orange in color; these are not very stable as a consequence of slow oxidation of the thiocyanate to sulfate. Nevertheless the rate of oxidation is not sufficiently great to account for the speed with which iodine dissolves, and the presence of appreciable concentrations of a somewhat stable intermediate species must be postulated. Furthermore, addition of concentrated potassium thiocyanate to a dilute solution of the triiodide-starch complex causes rapid decolorization of the characteristic blue color. If not too much thiocyanate has been added, however, the color can be restored by addition of iodide ion; this suggests existence of a reversible equilibrium between the triiodide ion and an iodine–thiocyanate complex.

The reaction between iodine and thiocyanate ion to produce sulfate and iodine cyanide has been known for many years.[3] In neutral or somewhat basic solutions it can be made to proceed quantitatively although several hours are required for completion of the oxidation. Griffith and McKeown[4] have studied the kinetics of this reaction and have proposed the existence of the intermediates I_2SCN^- and ISCN. In their paper mention is made of brief studies on the distribution of iodine between carbon tetrachloride and aqueous potassium thiocyanate which confirms the existence of the first of these species; a value of 0.009 at 25° is given for the equilibrium constant, $K = [CNS^-][I_2]/[CNS \cdot I_2^-]$.

Evidence for an iodine thiocyanate adduct also arises from investigations of the thiocyanate catalysis of the reaction between iodine and azide ion.[5] Here again, the existence of the intermediate species I_2SCN^- or ISCN has been postulated.

We have found that the reaction between iodine and thiocyanate ions in aqueous as well as several other solvent media yields a product which absorbs strongly in the ultraviolet region of the spectrum. Spectrophotometric studies have shown that under some conditions this substance is relatively stable, decomposing only slowly to give sulfate ions. We have concluded that the most probable composition of the product is I_2SCN^- and have evaluated the thermodynamic properties of this complex.

Experimental

Reagents and Solutions.—Standard NaSCN solutions were prepared from weighed quantities of the analytical reagent grade salt which had been recrystallized twice from methanol, washed with ether and dried at 130°. This treatment was necessary in order to remove iodine-consuming impurities. The recrystallization reduced the consumption of triiodide solution to less than 0.02 ml. of 0.01 *N* reagent by 5 g. of the solid when the standard ACS test was followed.[6]

Aqueous iodine solutions were prepared by shaking finely divided reagent grade I_2 with distilled water until nearly saturated solutions were obtained. These were standardized frequently against analytical reagent grade As_2O_3.

Sodium perchlorate solutions (about 9 *F*) were prepared by dissolving NaOH pellets in a minimum quantity of water, chilling and carefully neutralizing with 60% $HClO_4$ to litmus. Small amounts of hydrous ferric and aluminum oxides were removed by filtration and the solutions concentrated by boiling. Analyses of the solutions were made by evaporation of measured quantities and weighing of the anhydrous sodium perchlorate.

Perchloric acid solutions were prepared by dilution of the 60% reagent grade substance and standardization against sodium carbonate.

For the studies in ether solution, freshly opened cans of analytical reagent grade anhydrous ether were used for all preparations. Standard iodine solutions in this solvent were prepared just prior to their use by direct weighing of the reagent and dilution in a volumetric flask. Standard water solutions in ether were also prepared by direct weighing of deionized water and dilution. Anhydrous ether solutions of thiocyanic acid were prepared by extraction of an aqueous solution which was approximately 0.35 *N* in H_2SO_4 and 0.3 *N* in KSCN or NaSCN with an equal volume of freshly opened ether. After shaking for 2–3 minutes, the phases were allowed to separate and the

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[1] Support of this work by the National Science Foundation (Research Grant G-6277) is gratefully acknowledged.

[2] This paper is based upon portions of a thesis by Carl Lewis which has been submitted to the Graduate School of Stanford University in partial fulfillment of the requirements for the Ph.D. degree.

[3] E. Rupp and A. Schied, *Ber.*, **35**, 2191 (1902); A. Thiel, *ibid.*, 2766 (1902).

[4] R. O. Griffith and A. McKeown, *Trans. Faraday Soc.*, **31**, 875 (1935).

[5] F. Feigl, *J. Chem. Ed.*, **20**, 137 (1943); P. Senise, *J. Phys. and Colloid Chem.*, **55**, 1151 (1951).

[6] "Reagent Chemicals, American Chemical Society Specifications," American Chemical Society, Washington, D. C., 1950, p. 296.