Fig. 1.—Change in the catalytic activity of sample 4x with time (cyclohexanol dehydration reaction). Time of storage: curve 1, 1 day (105.2 mc./g.); curve 2, 315 days (8.5 mc./g.); curve 3, 503 days (1.9 mc./g.); curve 4, a nonradioactive sample stored for the same periods of time (the corresponding points are shown by open dots).

the surface of the crystals. On the other hand, there are reports[15] that preliminary heating of alumosilicate catalysts *in vacuo* increases their catalytic activity in the cracking of cumene, but subsequently their activity drops more quickly than that of the air-dried catalysts which were not vacuum-processed. Krohn and Wymer[1] heated their catalysts *in vacuo* while ours were air-dried.

In conclusion, it should be pointed out that we have also noted[16] a considerable increase in the rate of dehydration of isopropyl alcohol over radioactive tricalcium phosphate which contained isotopes Ca^{45} and P^{32}. There are cases, depending upon the nature of the catalyst and the reaction studied, in which the introduction of radioactive isotopes reduces the catalytic activity.[17] This, however, does not contradict the results obtained by us on cyclohexanol dehydration over the mixed catalyst $MgS^*O_4 + Na_2S^*O_4$.

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Specific Interactions of Optically Active Ions as Studied by Conductance

Sir:

The conductances of d- and l-tris(ethylenediamine)-cobalt(III) iodide $(Co(en)_3I_3)$ have been measured at 25° in water and in 0.003 M solutions of both d- and l-sodium tartrate in water. A significant difference in mobility was found between the two cobalt isomers in solutions of optically active tartrates.
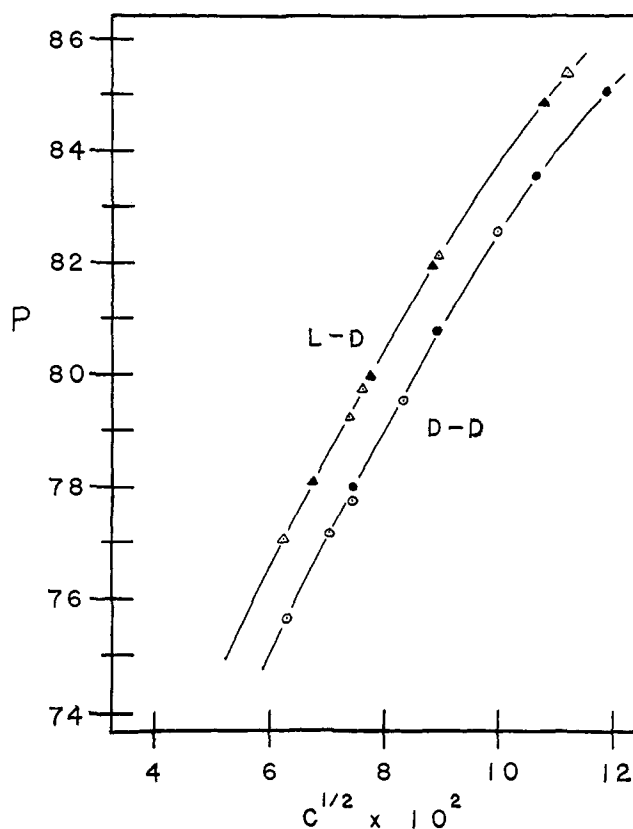

Fig. 1.—A plot of P vs. $c^{1/2} \times 10^2$ for the four samples of $Co(en)_3I_3$ in aqueous sodium d-tartrate solution. L–D and D–D label, respectively, curves for runs on the l-$Co(en)_3I_3$ and d-$Co(en)_3I_3$ in aqueous solution of sodium d-tartrate. The following symbols denote the four $Co(en)_3I_3$ samples used: $\triangle, l_1$; $\blacktriangle, l_2$; $\circ, d_1$; $\bullet, d_2$.

Instrumentation and techniques for conductance measurements made in pure water were similar to previously described methods and apparatus.[1] Conductances of the $Co(en)_3I_3$ isomers were measured in aqueous sodium tartrate by making dilution runs using portions of the same stock solution of sodium tartrate. It was thus possible to vary the concentration of the $Co(en)_3I_3$ without changing the sodium tartrate concentration. The d- and l-$Co(en)_3I_3$ samples prepared by the method of Dwyer[2] had specific rotations of +89.2° and −89.7°, respectively. Dwyer[3] reported $[\alpha]D$ +89° and −90° for the two isomers. To assure removal of traces of ionic impurities, the salts were carefully recrystallized three times from hot 50% ethanol–water solutions which had been filtered through sintered glass funnels. Partial racemization which occurred during the latter operation could easily be corrected for in the final calculations. Two samples of salt were prepared and purified. The final rotations were: d_1 ($[\alpha]D$ +73.5°), d_2 ($[\alpha]D$ +36.0°), l_1 ($[\alpha]D$ −79.4°), l_2 ($[\alpha]D$ −80.1°). Although sample d_2 was significantly racemized, it was run as a check on our method of correction for racemization. For conductance runs these slightly hygroscopic salts were dried to constant weight at 100° at 0.001 mm. and weighed on a microbalance in an air-tight weighing ampoule. Sodium d-tartrate (Powers-Weightman-Rosengarten Co., Analytical Chemicals, Philadelphia, Pa.) and sodium l-tartrate (Aldrich Chemical Co., Inc., Milwaukee, Wis.) were used without further purification.

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In pure water, plots of the equivalent conductance *vs.* the square root of concentration were identical within an average deviation of about 0.02% for the four separately prepared samples of $Co(en)_3I_3$. For the comparison of the conductances of *d*- and *l*-$Co(en)_3I_3$ in the sodium tartrate–water solvent, it was found convenient to define a function P, the apparent equivalent conductance, as

$$P_{d,l} = \frac{[\kappa_{d,l}(\text{solution}) - \kappa(\text{solvent})] \times 1000}{c}$$

where $\kappa_{d,l}$ (solution) is the measured specific conductance of a solution of *d*- or *l*-$Co(en)_3I_3$ at a concentration c (equivalents per liter) dissolved in the sodium tartrate–water solvent. The measured specific conductance of the pure sodium tartrate–water stock solvent is denoted κ (solvent). This function is the same as that for the usual definition of equivalent conductance, although in this case the solvent contributes quite significantly (from approximately 40 to 80%) to the total conductance. Even though the conductances of $Co(en)_3I_3$ and solvent are definitely not additive for this system, a plot of P *vs.* $c^{1/2}$ gives an accurate graphical comparison of the conductances of the two cobalt antipodes, since exactly the same solvent composition was used for each cobalt isomer. This plot would yield identical curves for the *d*- and *l*-$Co(en)_3I_3$ salts if there were no difference in their conductance behavior. The function P will, however, readily reveal differences in conductance between the two cobalt complex ions.

To correct for any racemization, one writes

$$P'_d = P_d X'_d + P_l X'_l \text{ and } P''_l = P_d X''_d + P_l X''_l$$

where P'_d is the measured P for the predominantly *d* cobalt salt sample, and P''_l is the measured P for the predominantly *l* cobalt salt sample, and X'_d, X'_l and X''_d, X''_l are mole fractions of *d*- and *l*-$Co(en)_3I_3$ isomers in the corresponding samples. The equations are then solved for P_d and P_l.

In Fig. 1 is shown a plot of P *vs.* $c^{1/2}$ for all samples of *d*- and *l*-$Co(en)_3I_3$ in 0.003 M sodium *d*-tartrate. The data for both the *d*-$Co(en)_3I_3$ samples are represented by curve D–D and the data for both *l* samples by L–D within an average deviation of about 0.04%. This excellent agreement confirms both the experimental technique and the method of correcting P for partial racemization. The most notable feature of Fig. 1 is that the essentially parallel plots differ by approximately 1.3 P units or 1.7%. This difference, which is much larger than the estimated maximum experimental error of 0.1%, definitely establishes that the mobility of *l*-$Co(en)_3I_3$ is greater than that of the corresponding *d* isomer in sodium *d*-tartrate aqueous solution. Thus, we may write the inequality D–D > L–D to represent the order of specific interactions in solution. Since such an inequality should remain valid when all ions are replaced by their optical antipodes, one would predict that L–L > D–L. To verify this, samples d_1 and l_1 were run in 0.003 M sodium *l*-tartrate. Here the mobility of the *d* isomer was indeed greater than that of the *l* isomer, and the magnitude of the effect (1.6%) was identical within experimental error with the difference for the sodium *d*-tartrate solution.

It is interesting to note that the solubility of the D–D compound is much less than for L–D, in fact, this is the way the salts are resolved.[2] This solubility difference may well be related to our results which show a sizable preferential interaction even in dilute solution.

The data on which these curves were based as well as further work now in progress will be presented in a later publication. It is hoped that these systems will serve as models for some instances of specific interaction among the more complex molecules found in biological systems.[4]

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Mössbauer Effect in *cis–trans* Isomers

Sir:

The study of resonant γ-ray spectroscopy (Mössbauer effect) has recently been extended to a number of closely related metal–organic compounds, especially those of iron[1,2] and tin.[3] The large amounts of data which have become available from these studies have been subjected to a number of correlations, such as that between quadrupole splitting (Q.S.) and isomer shift (I.S.) of Pettit and Collins,[4] and that of Herber, King, and Wertheim[5] which suggested that the isomer shift for iron–organic compounds could be treated as an additive molecular parameter. A prediction implicit in the latter interpretation is that the observed isomer shifts for iron atoms having the same local (nearest neighbor) environment but with different molecular structure in two or more compounds should be identical.

To test this prediction, we have examined the Mössbauer spectra of two *cis–trans* isomeric pairs. The experimental details are essentially identical with those reported earlier.[1,5] The source was prepared by diffusing previously electroplated Co^{57} into metallic copper for 3 hr. at 920–950°. This source showed an isomer shift of -0.374 ± 0.010 mm. sec.$^{-1}$ for an absorber of 0.5 mil 302 stainless steel at room temperature and -0.564 ± 0.010 mm. sec.$^{-1}$ for an absorber of $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ at room temperature. The motion was calibrated from the hyperfine spectrum[6] obtained using a 1.0 mil metallic iron absorber. The zero velocity point was determined from an independent Mössbauer experiment using a $Sn^{119m}O_2$

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