Table I. Second-Order Rate Constants of Hydrogen–Deuterium Exchange of Hydrocarbons

Hydrocarbon	k_2 (M^{-1} sec^{-1})
6[a,b]	0.50×10^{-2}
9[a,c]	0.15×10^{-2}
10[a,b,d]	0.33×10^{-2}
1[d,e]	2.0×10^{-3}
2[d,e]	0.7×10^{-7}

[a] Experiments were carried out at 25.0° in 87:13 DMSO-d_6–CH_3OD with CH_3ONa as the base. Rates are reproducible to less than ±10%. [b] Average of two runs. [c] Average of three runs. [d] The reported rate has been corrected for statistical factors. [e] The second-order rate constant for this compound has been computed on the basis of the data reported in ref 1a. Experiments were carried out at 60.0° in DMSO-d_6 with t-C_4H_9OK as the base.[1a]

H, $H_{2,4}$), 7.30 (m, 10 H, aromatic). Bicyclooctanone (**7**) was in turn reduced to the corresponding alcohol[7] **8**: mp 103–106°; ir 3420 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$) δ 1.09 (s, 1 H, OH), 2.04 (m, 6 H, H_8 and $H_{6,7}$), 2.73 (m, 2 H, $H_{1,5}$), 3.21 (m, 2 H, $H_{2,4}$), 4.69 (m, 1 H, H_3), 7.42 (m, 10 H, aromatic); mass spectrum[8] (relative intensities) 278 (M^+, 57%), 260 (3%), 171 (39%), 117 (41%), 91 (100%). Finally, alcohol **8** was dehydrated by means of thionyl chloride in pyridine to give 2,4-diphenylbicyclo[3.2.1]oct-2-ene[7] (**9**), in high yield; mp 53–55° from methanol; ^{1}H NMR ($CDCl_3$) δ 1.73 (m, 6 H, H_8 and $H_{6,7}$), 2.72 (m, 2 H, $H_{1,5}$), 4.03 (m, 1 H, H_4), 5.90 (m, 1 H, H_3), 7.33 (m, 10 H, aromatic); mass spectrum[8] (relative intensities) 260 (M^+, 27%), 219 (18%), 141 (39%), 130 (42%), 91 (100%).

The rates of base-catalyzed hydrogen–deuterium exchange of bicyclic hydrocarbons **6** and **9** as well as of *trans*-1,3-diphenylpropene[11] (**10**) were next examined. The latter compound was included as a reference system. The exchange experiments were carried out in 87:13 DMSO-d_6–CH_3OD containing CH_3ONa at 25°, and the deuterium uptake was monitored by mass spectroscopy.[12] The pseudo-first-order rate constants obtained experimentally were divided by the base concentration to afford the second-order rate constants shown in Table I.

Inspection of Table I shows that replacement of the hydrogens at C_2 and C_4 in bicyclic hydrocarbons **1** and **2** by phenyl groups has essentially eliminated the large rate difference of deuterium exchange between the two systems. Thus, while bicyclooctadiene (**1**) was found to exchange its allylic hydrogens $10^{4.5}$ times faster than monoene **2**, diphenylbicyclooctadiene (**6**) underwent deuterium exchange only 3.3 times faster than its saturated analogue **9**, strongly indicating that π electron participation in hydrocarbon **6** has been virtually totally eliminated. The slightly larger rate of bicyclic diene **6** relative to monoene **9** is most likely due to the stabilizing inductive effect of the $C_{6,7}$ double bond,[1a] rather than neighboring group effects. It should also be noted that the rates of both hydrocarbons **6** and **9** are in very close proximity to the exchange rate of *trans*-1,3-diphenylpropene, a system in which stabilization by means of neighboring group effects is not possible. On the basis of these results it can be concluded that just as in the case of carbonium ions, the extent of charge delocalization in carbanions has an inverse relationship to the stability rendered to the developing negative charge by groups directly attached to the carbanionic center.

With this principle, now firmly established for carbanions as well, its use as a tool in confirming the presence of long-range π electron participation in these intermediates should prove valuable.

Whether both phenyl groups are necessary for the elimination of electron participation in the carbanion derived from hydrocarbon **6** is not clear from the present study. The synthesis of a number of bicyclic systems whose exchange rates will help determine the minimum stabilization necessary to eliminate charge delocalization in this and other carbanions is currently under way.

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(7) Satisfactory elemental analysis was obtained for this new compound.
(8) Mass spectra were recorded using a DuPont 21-490 mass spectrometer.
(9) Peak assignments were based on spin decoupling and INDOR experiments, using a Varian XL-100 NMR instrument.
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(12) In a typical run, 3.86 mmol of bicyclic diene **6** was dissolved in 3.5 ml of DMSO-d_6 and 0.51 ml of CH_3OD in a 5-ml volumetric flask, and 0.03 ml of a 3.05 *M* stock solution of CH_3ONa in CH_3OD was added. The final base concentration after mixing was 1.83×10^{-2} *M*. The flask was immersed in a constant temperature bath at 25 ± 0.1°, and aliquots were withdrawn at varying time intervals over a period of 1.5 hr. The aliquots were quenched in a solution containing 10 ml of water and 1 ml of 3 *N* HCl and extracted with 30 ml of pentane. The organic solvent was dried and evaporated to give the partially deuterated diene **6**. The extent of deuterium incorporation was ascertained by low voltage mass spectroscopy.[8] The pseudo-first-order rate constant of the reaction was determined by plotting log H remaining vs. time. The second-order rate constants shown in Table I were obtained by dividing the pseudo-first-order rate constants by the base concentration.

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The Absolute Configuration of $(+)_D$-Trisphenanthrolinecobalt(III)

Sir:

In recent years Mason and co-workers[1-4] have extensively applied exciton theory, based on the strongly CD active, long-axis polarized π–π^* ligand transitions, to the assignment of absolute configuration for trisphenanthroline complexes. A possible objection to this approach is the apparent neglect of the metal ion and covalency.[5] In order to accommodate this possibility, Hawkins and co-workers[5-7] have proposed an alternative procedure, involving an analysis of both CD and isotropic absorption data. In several instances, absolute configurations based on the two methods differ, the most notable case being that of $(+)_D$-$Co(phen)_3^{3+}$. Whereas the former method[8] yields a ΛC_3 assignment, Hawkins et al.[5] suggest the ΔC_3 absolute configuration. The validity of the isotropic absorption analysis has recently been questioned,[9] but the controversy still remains unresolved.

We present here the results of an independent approach for examining this problem, where advantage is taken of the Pfeiffer effect displayed by trisphenanthroline complexes of divalent metal ions in the presence of S-$(-)_D$-malic acid. Kirschner et al.[10,11] have reported equilibrium solutions to be enriched in levo and dextro enantiomer (NaD line) for $\mathrm{Ni(phen)_3^{2+}}$ and $\mathrm{Fe(phen)_3^{2+}}$, respectively. Both isomers have been found to have the Δc_3 absolute configuration from x-ray diffraction studies.[12,13] The complex $\mathrm{Co(phen)_3^{2+}}$ also displays the Pfeiffer phenomenon in a malic acid environment,[10] with the levo isomer in excess. Kirschner[10] has suggested that this isomer also has the Δc_3 configuration. Provided this prediction is correct, oxidation of the latter equilibrium mixture should yield the thermally inert Δc_3 isomer of $\mathrm{Co(phen)_3^{3+}}$—thus providing the sign of its rotation at the D line.

Experimental conditions involved first preparing a N_2 purged aqueous solution 0.04 M in $\mathrm{Co(phen)_3^{2+}}$ and 0.3 M in $(-)_D$-malic acid. The solution was then transferred by syringe to a deaerated aqueous solution of either potassium dichromate or potassium permanganate (with oxidizing agent in 30% excess). In both instances, rapid oxidation to $\mathrm{Co(phen)_3^{3+}}$ ensued. The product solution was passed through a Dowex 1-X8 $\mathrm{Cl^-}$ exchange resin to remove malic acid and excess $\mathrm{MnO_4^-}$ or $\mathrm{Cr_2O_7^{2-}}$. Addition of a concentrated $\mathrm{NaClO_4}$ solution to the eluate precipitated $\mathrm{[Co(phen)_3](ClO_4)_3}$, which was filtered and washed copiously with $\mathrm{NaClO_4}$ solution and then ethanol. The relatively insoluble perchlorate salt was converted to the soluble chloride by shaking an aqueous suspension with Dowex 1-X8 ($\mathrm{Cl^-}$ form) and filtering. When $\mathrm{KMnO_4}$ was used as oxidant, the resultant solution displayed a negative NaD line rotation (−0.0364°, 0.008 M) employing a Bendix automatic polarimeter (Model 1144) with digital readout to ±0.0002°. The corresponding rotation for $\mathrm{K_2Cr_2O_7}$ as oxidant was −0.1100° (0.0147 M). It is noteworthy that no rotations were observed if $\mathrm{[Co(phen)_3](ClO_4)_2}$ was first precipitated from the Pfeiffer equilibrium mixture, followed by solid state chlorine oxidation of an ethanol suspension. Perchlorate anion most probably removes malic acid from the immediate complex environment prior to precipitation, resulting in racemization of the labile enriched enantiomer. Although this procedure was successful with $\mathrm{Ni(phen)_3^{2+}}$,[11] the relative inertness of the latter species would preclude racemization prior to precipitation.

In the present case involving rapid solution oxidation with $\mathrm{KMnO_4}$ and $\mathrm{K_2Cr_2O_7}$, the induced rotations were lost on addition of a small concentration of $\mathrm{Co(phen)_3^{2+}}$. This is consistent with the known rapidity of $\mathrm{Co(phen)_3^{2+/3+}}$ self-exchange[14] and fairly rapid racemization of $\mathrm{Co(phen)_3^{2+}}$ optical forms.[15] Furthermore, the optically active samples yielded CD spectra enantiomeric to that of a genuine sample of $(+)_D$-$\mathrm{Co(phen)_3^{3+}}$.[5,8] The rotations reported above indicated resolutions of 2.0 and 3.3% for $\mathrm{KMnO_4}$ and $\mathrm{K_2Cr_2O_7}$, respectively,[16] in keeping with that achieved earlier for $\mathrm{Ni(phen)_3^{2+}}$. These results, therefore, require a Λc_3 configuration for $(+)_D$-$\mathrm{Co(phen)_3^{3+}}$, an observation in agreement with the original assignment[8,9] by Mason and co-workers. The validity of the present approach, however, is dependent on the rate constants for oxidation of levo and dextro isomers of $\mathrm{Co(phen)_3^{2+}}$ being very similar in the presence of $(-)_D$-malic acid. This is probably a very reasonable assumption, in view of the reported absence of stereoselectivity in redox reactions involving transition metal systems.[17,18]

We note that the results reported above also have a significant bearing on the origin of the Pfeiffer phenomenon. The isolation of optically active $\mathrm{Co(phen)_3^{3+}}$ on oxidation of a $\mathrm{Co(phen)_3^{2+}}$-$(-)_D$-malic acid mixture provides further confirmation of a genuine displacement of enantiomer equilibrium in these solutions.

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Negative Ion Desorption Mass Spectrometry

Sir:

Application of field desorption mass spectrometry to the mass spectrometric analysis of thermolabile nonvolatile organic compounds[1] has demonstrated fairly high yields of molecular ions. We recently developed a new simpler field desorption source[2] and have demonstrated its use in the analysis of inorganic cations.[3] Field desorption per se is not an ionization process, but involves the desorption of ionic species previously present on a highly curved surface, which allows the buildup of high field gradients (10^7 to 10^8 V/cm). Therefore, it is conceivable that both cations and anions can be desorbed, depending on the polarity of the field desorption source.

This communication presents a series of preliminary results on the mass spectrometry of inorganic *anions* produced by field desorption. The ionization source and the mass spectrometric system have been described previously.[2,3] The desorption takes place from a freshly broken tungsten surface situated about 50 μm from a slit counter electrode (anode in this case). Tungsten rod of $^1/_{16}$-in. diameter was notched at 1-in. intervals on an abrasive wheel and