the absolute configuration of the γ-carbon in both sultones as well as both sultines is the same. In conclusion, we suggest that γ-sultines **9A-12A** and **9B-12B** (Chart I, Table II) may be assigned the $(R)^{C}$-$(S)^{S}$ and $(R)^{C}$-$(R)^{S}$ absolute configurations, respectively.

Registry No. (*R*)-(+)-**1**, 42969-65-3; (*S*)-(−)-**1**, 2914-69-4; (−)-**2**, 84064-97-1; (+)-**2**, 84107-52-8; (*R*)-(−)-**7**, 84064-98-2; (*R*)-(−)-**8**, 84073-44-9; **9A**, 84107-53-9; **9B**, 84107-54-0; **10A**, 84064-99-3; **10B**, 84107-55-1; **11A**, 84065-00-9; **11B**, 84107-56-2; **12A**, 84065-01-0; **12B**, 84107-57-3.

Mechanism of Proton Removal from Intramolecularly Hydrogen-Bonded (Phenylazo)resorcinol Monoanions

Frank Hibbert* and Gareth R. Simpson

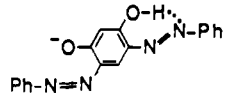
Department of Chemistry, King's College London Strand, London WC2R 2LS, England

Received July 1, 1982

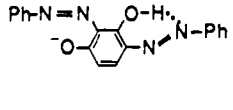
Two mechanisms have been proposed[1,2] for removal of the intramolecularly hydrogen-bonded proton from 4-phenylazoresorcinol monoanion. The mechanisms, Schemes I[1] and II[2], were based on measurements of the reciprocal relaxation time (τ^{-1}) for equilibration of the monoanion and dianion in the presence of hydroxide ion after a temperature perturbation. As the hydroxide ion concentration was varied, a minimum in the value of τ^{-1} was found as opposed to the expected linear variation.

Scheme I involves direct attack of hydroxide ion on the internally hydrogen-bonded monoanion (upper path) and a two-step process through an open form of the monoanion (lower path).[1] For other hydrogen-bonded acids it has been shown[3] that proton transfer occurs by the two-step process, and there is no evidence for direct attack on hydrogen-bonded protons. This makes Scheme I of particular interest. An alternative explanation for the unusual dependence of τ^{-1} on hydroxide ion concentration is shown in Scheme II. In the lower path, protonation of the monoanion gives a low concentration of the conjugate acid, and this is followed by formation of an isomeric form of the monoanion in which the proton is located in a site where it is unable to participate in an intramolecular hydrogen bond. The upper route involves proton removal from the monoanion by either direct attack on the hydrogen-bonded proton or by two-step reaction through an open form; the precise mechanism cannot be specified.[4]

We now report a similar dependence of reciprocal relaxation time on hydroxide ion concentration for proton removal from bis(phenylazo)resorcinol monoanions **1** and **2**.[5] Relaxation times



1



2

for the equilibration between monoanions **1** and **2** and their respective dianions in the presence of hydroxide ion were determined at 5 °C and 0.2 M ionic strength in aqueous solution by using the temperature-jump technique. The reaction was followed spectrophotometrically at ca. 520 or 440 nm, corresponding to absorbance by the dianion and monoanion, respectively. The results for **2** are given in Figure 1, and it is clear that a minimum in τ^{-1} is observed.

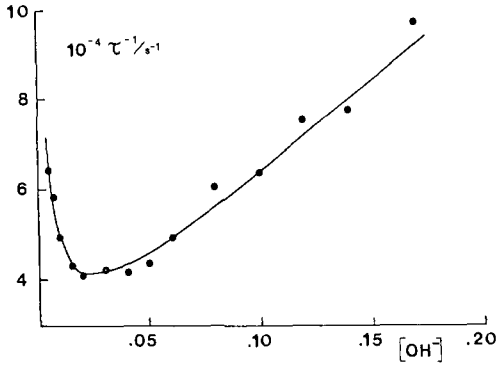
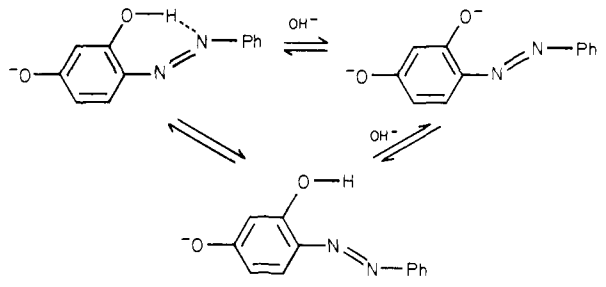
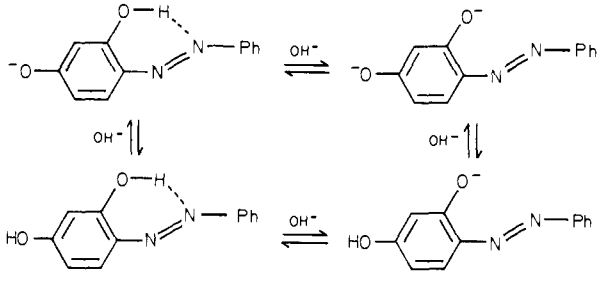


Figure 1. Dependence of reciprocal relaxation time for the equilibration between the monoanion and dianion of 2,4-bis(phenylazo)resorcinol on hydroxide ion concentration. The line is a best fit of eq 1.

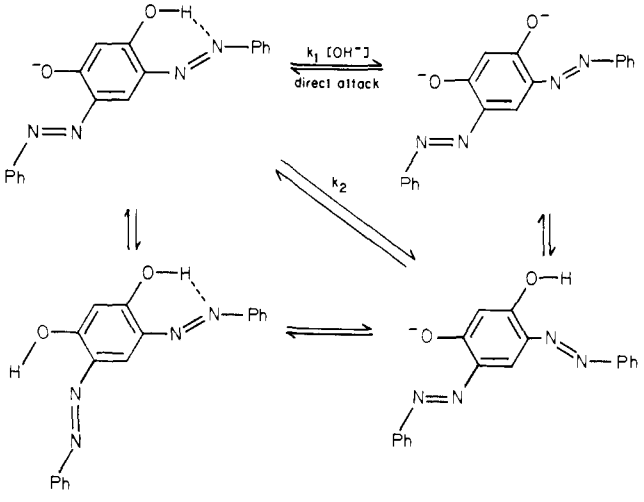
Scheme I



Scheme II



Scheme III



Certain simplifications are possible for the bis(phenylazo)-resorcinol monoanions in attempting to explain the minimum in terms of Schemes I and II. This arises because for **1** and **2** an intermediate cannot be written where the proton is located at a site in which it is unable to participate in an intramolecular hydrogen bond. This means that if the proton is relocated in **1**

(1) Perlmutter-Hayman, B.; Sarfaty, R.; Shinar, R. *Int. J. Chem. Kinet.* **1976**, *8*, 741–751.
(2) Yoshida, N.; Fujimoto, M. *Chem. Lett.* **1977**, 1301–1304.
(3) Hibbert, F.; Awwal, A. *J. Chem. Soc., Perkin, Trans. II* **1978**, 939–945. Hibbert, F.; Robbins, H. J. *J. Am. Chem. Soc.* **1978**, *100*, 8239–8244. Kresge, A. J.; Powell, M. F. *Ibid.* **1981**, *103*, 972–973.
(4) If the upper route in Scheme II occurs by two-step reaction through an open form, it is necessary that this open form and the intermediate isomeric form of the monoanion on the lower route should differ significantly in energy in order to explain the kinetic behavior. The alternative possibility is that the upper route in Scheme II involves direct single-step attack. These arguments will be presented in detail when a full report of this work is published.
(5) Hodson, H. F.; Stamm, O. A.; Zollinger, H. *Helv. Chim. Acta* **1958**, *41*, 1816–1823.

0002-7863/83/1505-1063$01.50/0

the result is an intermediate that is either identical with the original monoanion or to an open form of the original monoanion. The latter is the intermediate that is postulated in Scheme I, and the two schemes then become very similar. These combined mechanistic possibilities are shown in Scheme III. Equation 1 is

$$\tau^{-1} = (k_2 + k_1[OH^-])(1 + 1/K[OH^-]) \quad (1)$$

derived[1,2] from Scheme III and the line in the figure is a plot of eq 1 with the values $k_1 = 4.1 \times 10^5$ M^{-1} s^{-1}, $k_2 = 7.4 \times 10^3$ s^{-1}, and $K = 32.0$ M^{-1}. The value of the equilibrium constant K = [dianion]/[monoanion][OH^-] = 32.0 ± 2 M^{-1} was determined separately by spectrophotometric measurements.[6]

Scheme III is identical with Scheme I except that an additional route to the open form of the monoanion through the conjugate acid is included. Formation of the open form can occur either by direct opening or through the conjugate acid. In order to explain the dependence of reciprocal relaxation time on hydroxide ion concentration and derive eq 1, it is necessary to specify that the upper route in Scheme III occurs by direct attack on the hydrogen-bonded proton and does not proceed through an open form of the monoanion.[7] In this way Scheme III differs from Scheme II, and the data for bis(phenylazo)resorcinol monoanions therefore provide evidence that direct attack by base on the hydrogen-bonded proton is occurring.

Acknowledgment. Support from the SERC and Royal Society is gratefully acknowledged.

Registry No. 1, 84174-81-2; **2**, 84237-51-4.

(6) For **1** half-dissociation occurs at [OH^-] = 0.0002, and kinetic data were restricted to the range [OH^-] = 0.0005–0.004 M. A linear dependence of τ^{-1} on [OH^-] was observed, but the gradient and intercept were not compatible with the separately measured equilibrium constant. The data were fitted to eq 1, and it was predicted that the minimum was below the lowest accessible hydroxide ion concentration.

(7) If the upper route in Scheme III occurred through the open form of the monoanion, two of the routes in Scheme III would become identical. The expression derived for the dependence of τ^{-1} on [OH^-] from the resulting scheme is not compatible with a minimum in τ^{-1}.

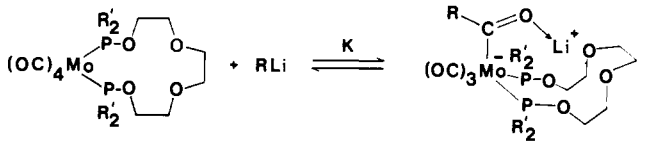
Phosphorus Donor-Crown Ether Hybrid Ligands as a Route to CO Activation: Phosphorus Substituent Effects and the Importance of Strong Cation Binding

John Powell,* Michael Gregg, Anda Kuksis, and Patty Meindl

Department of Chemistry, University of Toronto Toronto, Ontario, Canada M5S 1A1

Received September 14, 1982

We have recently shown that "selective cation binding by the product molecule" may provide additional stabilization with respect to the addition of a nucleophile to a coordinated carbon monoxide[1] (e.g., reaction 1). In this communication we present data that clearly emphasize the importance of strong Li^+ cation binding in promoting nucleophilic addition to coordinated CO.



1a-d reaction 2 reaction 1

(a) R' = Ph
(b) R'_2 = $-OCH_2CH_2O-$
(c) R'_2 = $1,2-OC_6H_4O-$
(d) R'_2 = $-N(Me)C_2H_4(Me)N-$

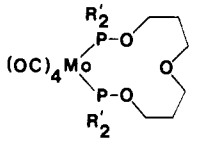
(1) Powell, J.; Kuksis, A.; May, C. J.; Nyburg, S. C.; Smith, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 5941.

Table I. Infrared Data (ν_{CO} Region) and Selected Equilibrium Constant Data {K = [$Mo(CO)_3(PhCOLi)P_2$]/([$Mo(CO)_4P_2$][RLi])} As Determined by Infrared Spectroscopy (ν_{CO} Region) for Reaction 1 in THF Solutions (7.25×10^{-3} M in Mo) at 25 °C

complex	ν_{CO}, cm^{-1}	equilibrium const,[a] L mol^{-1} $K(PhLi)_{THF}$	$K(MeLi)_{THF}$
1a	2024, 1928, 1909, 1899	2700	44000
1b	2039, 1947, 1928	<5	<5
1c	2052, 1966, 1948	<1	<5
1d	2021, 1917, 1907, 1883	3000	100000
3a	2024, 1923, 1910, 1899	500	6700
3b	2041, 1952, 1928	<50	<50
3c	2075, 1990, 1970, 1950	<5	<50
3d	2020, 1918, 1906, 1886	2900	11000

[a] Errors in individual K value vary from ±40% to ±15% depending on the magnitude of K (largest and smallest values have higher percent errors).

Replacing the phenyl substituents on the phosphorus atoms in **1a** with more electron-withdrawing substituents could have two *competing* effects that would influence the magnitude of the equilibrium constant for reaction 1: (i) It would make the coordinated CO in **1** more susceptible to nucleophilic attack (i.e., decrease the electron density on the CO carbon as indicated by slightly higher ν_{CO}'s, and/or (ii) it would result in the product **2** being a poorer ligand for Li^+ by decreasing the basicity of the "P–O donor oxygen" (i.e., increased oxygen to phosphorus π-dative bonding). To determine which of these effects is the more important, we have synthesized the tetracarbonyl phosphite–crown ether molybdenum complexes **1b,c** and **3b,c** via previously reported



3a-d

methods.[1,2] Equilibrium constant data for the reaction of these compounds with organolithium reagents (i.e., K, reaction 1) are given in Table I together with those for their diphenylphosphinite analogues **1a** and **3a**. The data indicate that the phosphite systems do not favor nucleophilic addition to a coordinated CO owing to the reduced basicity of the P–O donor oxygen, which makes the products of nucleophilic addition (e.g., **2b,c**) poorer ligands for Li^+ as compared to the diphenylphosphinite analogues (e.g., **2a**). Replacement of two of the phosphite oxygens with dialkylamino groups, as in complexes **1d** and **3d**, should lead to an increase in the basicity of the remaining oxygen (NB strong nitrogen to phosphorus π-dative bonding[3]) and hence make **2d** thermodynamically more favorable owing to the stronger Li^+ binding by this molecule. The equilibrium constant data (table) indicate that this is so. (N.B. For **1a–d** and **3a–d** it is the complexes with the *lowest* ν_{CO}'s that are most susceptible to nucleophilic addition to a coordinated CO.)

That "strong Li^+ binding by the product molecule" is a dominant feature in determining the extent of nucleophilic addition to a coordinated CO in *cis*-$(OC)_4M(PR_3)_2$ complexes is also illustrated by a study of the molecules **4** and **5**. Complex **4** (Scheme I) is totally unreactive with respect to RLi addition. In contrast **5** reacts sequentially with 2 equiv of RLi in THF to give the highly reactive dilithium salt **6** (may be isolated as a yellow solid). Addition of a third equivalent of RLi results in an orange-red solution, and IR and ^{13}C NMR data are consistent with the formation of the acylate product **7**.[4] Addition of 1 equiv of

(2) Satisfactory infrared and ^1H, ^{13}C, and ^{31}P NMR spectra and elemental analyses have been obtained for all the new *cis*-tetracarbonyl complexes reported in this communication.

(3) Grec, D.; Hubert-Pfalzgrat, L. G.; Riess, J. G.; Grand, A. *J. Am. Chem. Soc.* **1980**, *102*, 7133 and references therein.

0002-7863/83/1505-1064$01.50/0