(10) P. D. Bartlett and A. P. Schaap, *J. Am. Chem. Soc.*, **92**, 3223 (1970).
(11) M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **97**, 3978 (1975).
(12) D. B. Sharp, Abstracts, 138th National Meeting of the American Chemical Society, New York, N.Y., Sept 1960, p 79P; P. D. Bartlett, private communication, 1974.
(13) G. B. Schuster, N. J. Turro, H. Steinmetzer, A. P. Schaap, G. Faler, W. Adam, and J. C. Liu, *J. Am. Chem. Soc.*, **97**, 7110 (1975).
(14) (a) H. E. O'Neil and W. H. Richardson, *J. Am. Chem. Soc.*, **92**, 6553 (1970); (b) W. H. Richardson, F. C. Montgomery, M. B. Yelvington, and H. E. O'Neil, *ibid.*, **96**, 7525 (1974).
(15) T. Wilson, unpublished work.
(16) N. J. Turro, P. Lechtken, G. Schuster, J. Orell, H. C. Steinmetzer, and W. Adam, *J. Am. Chem. Soc.*, **96**, 1627 (1974).
(17) T. R. Darling and C. S. Foote, *J. Am. Chem. Soc.*, **96**, 1625 (1974).
(18) Enthalpies for thermolysis of solid-phase tetramethyldioxetane have been reported[19] but gas phase results are not available.
(19) P. Lechtken and G. Höhne, *Angew. Chem., Int. Ed. Engl.*, **12**, 772 (1973).
(20) T. H. Dunning and P. J. Hay, "Modern Theoretical Chemistry: Electronic Structure", Vol. II, H. F. Schaefer III, Ed., Plenum Press, New York, N.Y., 1976, in press.
(21) Dioxetane was assumed to have C_{2v} symmetry, the C-H bond lengths were fixed at 1.08 Å. All other geometry parameters were optimized using STO-4G HF wavefunctions. The ring bond lengths were then further optimized at the DZd GVB(4) level (where the four C-C, C-O, and O-O bonds were correlated. A similar procedure was used for peroxirane.
(22) D. R. Stull and H. Prophet, JANAF Thermochemical Tables, NSRDS-NBS 37, U.S. Government Printing Office, Washington, D.C., 1971.
(23) M. J. S. Dewar, R. C. Hadden, W. K. Li, W. Thiel, and P. K. Weiner, *J. Am. Chem. Soc.*, **97**, 4540 (1975).
(24) S. W. Benson, "Thermodynamic Kinetics", Wiley, New York, N.Y., 1968.
(25) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1302 (1975).
(26) S. W. Benson and H. E. O'Neil, "Kinetic Data on Gas Phase Unimolecular Reactions", NSRDS-NBS 21, U.S. Government Printing Office, Washington, D.C., 1970.
(27) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y., 1970.
(28) L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **95**, 693 (1973).
(29) T. Wilson and A. P. Schaap, *J. Am. Chem. Soc.*, **93**, 4126 (1971).
(30) B. J. Moss, F. W. Bobrowicz, and W. A. Goddard III, *J. Chem. Phys.*, **63**, 4632 (1975).
(31) This is assuming the C-O bond strength of dioxetane to be that of a typical peroxide (70 kcal) minus the calculated dioxetane ring strain energy (24 kcal).
(32) These numbers suggest that formation of the CCOO biradical from C_2H_4 and O_2 is only 9 kcal endothermic. The activation energy for forming this biradical should be significantly larger.
(33) M. J. S. Dewar and S. Kirschner, *J. Am. Chem. Soc.*, **96**, 7578 (1974).
(34) C. W. Eaker and J. Hinze, *Theor. Chim. Acta*, **40**, 113 (1975).
(35) C. W. Eaker and J. Hinze, *J. Am. Chem. Soc.*, **96**, 4084 (1974).
(36) Since only heats of atomization using CNDO-MCSCF were reported, the estimates of bond strengths were necessarily approximate. For the C-C bond bond strength of C_2H_6, we assumed the error in each C-H bond strength to be equal to the average error in the CH_4 atomization energy. The remaining error was then assumed to be in the C-C bond strength. A similar analysis of the heats of atomization of H_2O_2 and H_2O gave the estimated error in O-O bond strengths.

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Hydroxide Ion as a "Non-Innocent" Quencher of the Photoaquation Reaction of Chromium(III) Complexes

Sir:

Several Cr(III) complexes are known to exhibit appreciable phosphorescence under experimental conditions (fluid solutions near room temperature) in which photochemistry is usually observed.[1] For these complexes the comparison of the phosphorescence and photolysis quenching[2-10] or sensitization[11-13] has led to important progress in the understanding of the excited-state behavior. Quenching and sensitization processes involve an intimate interaction between the excited molecule and the quencher.[14] Such an interaction may result in physical events (e.g., electronic energy transfer, spin-catalyzed deactivation, etc.) or in some kind of chemical reaction between the excited state and the quencher (e.g., electron transfer, hydrogen transfer, etc.). In the latter case new chemical species are formed which exhibit their own chemical reactivity. This may cause complications in the analysis of the experiment and may also lead to erroneous mechanistic conclusions.

Table I. Quenching of the *t*-$Cr(en)_2(NCS)_2^+$ Phosphorescence Emission[a]

Quencher[b] (kK)	k_q,[c] $M^{-1}\ s^{-1}$	Quenching mechanism
$Ni(gly)_2$[d] (10)[e]	7.5×10^7	Energy transfer
$Co(NH_3)_5Cl^{2+}$ (11.4)[e]	1.8×10^8	Energy transfer
$Cr(CN)_6^{3-}$[f] (12.3)[g]	2.3×10^9	Energy transfer
$Co(CN)_6^{3-}$ (~18)[h]	$<1 \times 10^5$	
I^- (44)[i]	$<1 \times 10^5$	
OH^-[j] (54)[i]	1.3×10^8	Chemical reaction[k]

[a] Air equilibrated aqueous solution, 15 °C, complex concentration 1×10^{-2} M, pH 3, unless otherwise stated. [b] The energy of the lowest excited state is given in brackets. [c] Bimolecular quenching constant obtained from the Stern–Volmer plot $I^0/I = 1 + k_q\tau[Q]$; $\tau = 10.5\ \mu s$. [d] Natural pH. [e] C. K. Jørgensen, *Adv. Chem. Phys.*, **5**, 33 (1963). [f] Lifetime quenching measurements showed that static quenching is negligible. [g] From ref 12. [h] J. N. Demas and J. W. Addington, *J. Am. Chem. Soc.*, **98**, 5800 (1976). [i] M. Fox, in "Inorganic Photochemistry", A. W. Adamson and P. D. Fleischauer, Ed., Wiley, New York, N.Y., 1975, p 333. [j] Phosphate buffer, 0.05 M. [k] See text.

We have studied the phosphorescence and photoreaction (NCS^- release)[15] quenching of *trans*-$Cr(en)_2(NCS)_2^+$ (en, ethylenediamine) and have found that OH^-, which is currently used in investigations of this kind,[5,9] causes anomalous results for the quenching of the photoreaction.

Phosphorescence and photolysis studies were carried out in air equilibrated aqueous solutions at 15 °C with 508-nm excitation using apparatus and techniques previously described.[18] The species $Ni(gly)_2$ (gly, glycinato ion), $Co(NH_3)_5Cl^{2+}$, $Cr(CN)_6^{3-}$, $Co(CN)_6^{3-}$, I^-, and OH^- were used as potential quenchers. The results obtained in the quenching of the *trans*-$Cr(en)_2(NCS)_2^+$ phosphorescence are summarized in Table I. As the energy level of the ^2E emitting state of *trans*-$Cr(en)_2(NCS)_2^+$ is 13.8 kK above the ground state,[1] quenching via electronic energy transfer is thermodynamically allowed for $Ni(gly)_2$, $Co(NH_3)_5Cl^{2+}$, and $Cr(CN)_6^{3-}$, whereas it is forbidden for $Co(CN)_6^{3-}$, I^-, and OH^-. Nevertheless, OH^- does quench the *trans*-$Cr(en)_2(NCS)_2^+$ phosphorescence with a relatively high rate constant. In parallel experiments the quenching of the NCS^- photoaquation reaction was investigated[19] and it was found that a fraction of the photoreaction quantum yield (Φ_{NCS^-}) was unquenchable under conditions of total phosphorescence quenching. Plots of $\Phi_{NCS^-}/\Phi^0_{NCS^-}$ against I/I^0 [7] revealed that the data obtained for $Ni(gly)_2$, $Co(NH_3)_5Cl^{2+}$, and $Cr(CN)_6^{3-}$ fall on the same straight line, whereas those concerning OH^- fall on a different straight line (Figure 1). Specifically, the results obtained with $Ni(gly)_2$, $Co(NH_3)_5Cl^{2+}$, and $Cr(CN)_6^{3-}$ show that the unquenchable part of the photoreaction is ~20%, whereas the results obtained with OH^- would indicate that the unquenchable part is ~55%. Since the fraction of unquenchable photoreaction has important mechanistic implications as a measure of the "prompt" quartet reaction,[2-10,14] it is necessary to know which of the two values is the right one. There seems to be little doubt that the right value is that obtained with $Ni(gly)_2$, $Co(NH_3)_5Cl^{2+}$, and $Cr(CN)_6^{3-}$, which are expected to quench by a chemically "innocent" mechanism, i.e., electronic energy transfer. The quenching by OH^-, on the contrary, has to take place by means of some kind of chemical reaction.

For the quenching of $(^2E)Cr(NH_3)_6^{3+}$ by OH^-, Langford and Tipping[5] suggested the involvement of an amine-hydrogen deprotonation step. This mechanism was also considered likely for hydroxide quenching of $(^2E)Cr(en)_3^{3+}$,[9] but it seems to be less probable in our case owing to the lower positive charge of

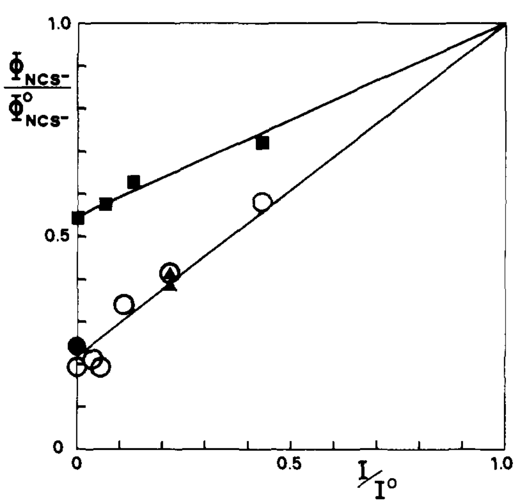

Figure 1. Plot of $\Phi_{NCS^-}/\Phi^0_{NCS^-}$ against I/I^0. The quenchers used were OH^- (■), $Ni(gly)_2$ (●), $Co(NH_3)_5Cl^{2+}$ (▲), and $Cr(CN)_6^{3-}$ (○).

the complex. A more reasonable mechanism seems that involving the formation of a seven-coordinate intermediate containing OH^- in the coordination sphere. Whatever the intimate mechanism of hydroxide quenching, our results show that the interaction between (^2E)- *trans*-$Cr(en)_2(NCS)_2^+$ and OH^- quenches the "intrinsic" manifestations (including phosphorescence emission and NCS^- aquation[20]) of the ^2E excited state, but introduces a new path for NCS^- aquation from ^2E. As there is no reason why this could not occur for other complexes,[21] the use of OH^- as a selective doublet quencher[5,9] in mechanistic studies of Cr(III) photochemistry should be avoided.[22,23]

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References and Notes

(1) N. A. P. Kane-Maguire and C. H. Langford, *J. Chem. Soc., Chem. Commun.*, 895 (1971).
(2) S. N. Chen and G. B. Porter, *Chem. Phys. Lett.*, **6**, 41 (1970).
(3) G. B. Porter, S. N. Chen, H. L. Schlafer, and H. Gausmann, *Theor. Chim. Acta*, **20**, 81 (1971).
(4) N. A. P. Kane-Maguire and C. H. Langford, *J. Am. Chem. Soc.*, **94**, 2125 (1972).
(5) C. H. Langford and L. Tipping, *Can. J. Chem.*, **50**, 887 (1972).
(6) H. F. Wasgestian, *J. Phys. Chem.*, **76**, 1947 (1972).
(7) R. Ballardini, G. Varani, H. F. Wasgestian, L. Moggi, and V. Balzani, *J. Phys. Chem.*, **77**, 2947 (1973).
(8) N. A. P. Kane-Maguire and C. H. Langford, *Inorg. Chem.*, **15**, 464 (1976).
(9) N. A. P. Kane-Maguire, J. E. Phifer, and C. J. Toney, *Inorg. Chem.*, **15**, 593 (1976).
(10) M. Maestri, F. Bolletta, L. Moggi, V. Balzani, M. S. Henry, and M. Z. Hoffman, *J. Chem. Soc., Chem. Commun.*, in press.
(11) V. Balzani, R. Ballardini, M. T. Gandolfi, and L. Moggi, *J. Am. Chem. Soc.*, **93**, 339 (1971).
(12) N. Sabbatini and V. Balzani, *J. Am. Chem. Soc.*, **94**, 7587 (1972).
(13) N. Sabbatini, M. A. Scandola, and V. Carassiti, *J. Phys. Chem.*, **77**, 1307 (1973).
(14) V. Balzani, L. Moggi, M. F. Manfrin, F. Bolletta, and G. S. Laurence, *Coord. Chem. Rev.*, **15**, 321 (1975).
(15) *trans*-$Cr(en)_2(NCS)_2^+$ undergoes two distinct photoreactions, i.e., NCS^- release and detachment of an ethylenediamine end.[16] In this note we are only dealing with the former reaction which is the predominant one. A systematic study of the photochemical and photophysical behavior of this complex will be reported elsewhere.[17]
(16) C. Bifano and R. G. Linck, *Inorg. Chem.*, **13**, 609 (1974).
(17) Manuscript in preparation.
(18) R. Ballardini, G. Varani, L. Moggi, V. Balzani, K. R. Olson, F. Scandola, and M. Z. Hoffman, *J. Am. Chem. Soc.*, **97**, 728 (1975).
(19) Spectrophotometric measurements (after acidification for the alkaline solutions) showed that the photoreaction products were the same under all the experimental conditions used; free NCS^- determinations showed that the reaction products were stable toward NCS^- release for time periods of our experiments both in acid and alkaline solutions.
(20) By analogy with other Cr(III) complexes,[2,4,5,7-9] this reaction could take place from $^4T_2$ after $^2E \rightarrow {}^4T_2$ back-intersystem crossing.
(21) For $Cr(NH_3)_6^{3+}$, preliminary experiments with $Ni(gly)_2$ as a quencher have shown that the unquenchable part of the photoreaction is 50%; this value is noticeably lower than that obtained[5] by OH^- quenching (80–90%).
(22) For $Cr(phen)_3^{3+}$,[8] phosphorescence quenching by OH^- is accompanied by an *increase* in the quantum yield of the photoreaction. According to our mechanism, this result is expected when the new reaction path opened by the interaction between ^2E and OH^- is more efficient than the "intrinsic" ^2E reaction.
(23) For $Cr(en)_3^{3+}$, quenching by $CoCl_2$[7] and OH^- [9] seems to lead to approximately the same value for the fraction of unquenchable photoreaction. This means that in this case the interaction between ^2E and OH^- does not lead to an appreciable amount of photolysis products.

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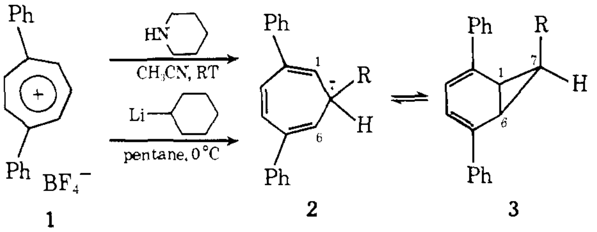
Effect of a C_7 π-Electron Donor on a Cycloheptatriene-Norcaradiene Equilibrium

Sir:

π-Electron donors in a bisected conformation at the C_7 (cyclopropyl) position are believed to destabilize norcaradienes either by weakening the C_1-C_6 bond through HOMO-LUMO interactions[1,2] or by repulsion between filled π-electron energy levels.[3] The validity of this theory not only bears on our understanding of cycloheptatriene and cyclopropane properties, but also on our fundamental understanding of resonance. We now report the first experimental evidence which demonstrates that replacement of hydrogen at C_7 with a π donor substituent can stabilize the norcaradiene form relative to the cycloheptatriene form and discuss possible explanations for this behavior.

Our approach has been to investigate the effect of a good donor group (the piperidino group) and the sterically equivalent[4,5] cyclohexyl group at C_7 on a closely balanced cycloheptatriene-norcaradiene equilibrium.[6,7] Pale yellow crystals (mp 120 °C dec, presumably **3a**)[8] were obtained in 94% yield on treatment of **1** with piperidine. Spectroscopic data indicated the rapidly equilibrating **2a** ⇌ **3a** in solution: UV $\lambda_{max}^{CH_3CN}$ 273 (ϵ 21 400), 353 nm (8150); NMR (CCl_4, 25 °C) δ 7.24 (m, 10 H, phenyl), 6.76 (s, 2 H, $H_{3,4}$), 4.45 (d, 2 H, $H_{1,6}$, J_{17} = 4.8 Hz), 2.72 (m, 4 H, NCH_2), 1.80 (t, H_7, J_{17} = 4.8 Hz), and 1.57 (m, methylene) (the latter two m 7 H together). Treatment of **1** with cyclohexyllithium afforded **2b** ⇌ **3b** in 8% yield. The latter were separated from their 7-cyclohexyl-1,5-diphenylcycloheptatriene (mp 143–144 °C) and 7-cyclohexyl-1,4-diphenylcycloheptatriene isomers, each formed in 17% yield, by elution with pentane on neutral alumina and on 40% silver nitrate on silica gel followed by selective crystallization from pentane-ether-methanol: white crystals; mp 123–125 °C (presumably **3b**);[8] UV λ_{max}^{hexane} 241 (ϵ 37 100), 322 nm (8750); NMR (CS_2, 25 °C) δ 7.25 (10 H, phenyl), 6.92 (s, 2 H, H_3 and H_4), 4.75 (d, 2 H, H_1 and H_6, J_{17} = J_{67} = 5.5 Hz), and 0.5–2.3 (m, 12 H, H_7 and cyclohexyl). In CCl_4 at 25 °C $H_{1,6}$ absorb at δ 4.88.



a, R = 1-piperidino
b, R = cyclohexyl
c, R = H

The time-averaged values of $\delta_{H_{1,6}}$ in **2a** ⇌ **3a** (4.45) and **2b** ⇌ **3b** (4.88) indicate that, in contrast to **2c** (5.74),[6,7] substantial quantities of the norcaradiene form are present in both