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Ligand Redistribution in Triazene 1-Oxide Complexes: A Voltammetric Study

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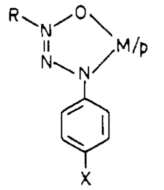

$M(RX)_p$

M = Cu, p = 2

M = Co, Fe, Ru ; p = 3

R = Et , Ph

X = OMe, Me, H, Cl, CO_2Et , NO_2

Mixed complex formation via redistribution reactions is of much import in chemistry,[1,2] and in the case of electroactive species voltammetry is a useful technique for product identification.[3,4] Triazene 1-oxides afford neutral complexes (abbreviated as $M(RX)_p$) that undergo[5,6] the exactly or nearly reversible metal-centered electron-transfer reaction 1 whose

$$M(RX)_p + e^- \rightleftharpoons M(RX)_p^- \qquad (1)$$

formal potential can be offset by R and finely controlled by X. We thus have an unique opportunity of utilizing reaction 1 as a probe for monitoring the possible ligand redistribution reaction 2 in which the various species subtly differ only in substituents X and/or R. This aspect is explored in the present work.

$$M(RX)_p + M(R'X')_p \rightleftharpoons M(RX)_{p-1}(R'X') + \ldots + M(RX)(R'X')_{p-1} \qquad (2)$$

Results and Discussion

Choice of Mixtures. Equimolecular amounts of parent species having sufficiently divergent formal potentials (to facilitate voltammetric product detection) are used to prepare the mixtures that are identified by letters **a–l** as in Table I. Mixed complexes are identified by numbers **1–26** as in Table II. The mixed complexes **12** and **18** were considered earlier.[5]

In general the presence of mixed complex(es) is revealed by the appearance of new response(s) in addition to those of the parent species. In all cases (**a–l**) redistribution equilibrium was found to be readily achieved at room temperature. Several ruthenium mixtures were also scanned but without any evidence of redistribution within 24 h of mixing.

Additivity Rule and Hammett Correlation. Representative voltammograms are in Figures 1 and 2. The observed formal potentials ($E°_{298}$ referenced to SCE) of parent and mixed species are collected in Tables I and II. The $E°_{298}$ values of the mixed species show very good agreement (Table II) with values calculated on the assumption that each RX chelate ring contributes the quantity $E°(RX)$ defined by eq 3 to the formal

$$E°(RX) = E°_{298}(M(RX)_p)/p \qquad (3)$$

potential of the mixed complex. In eq 3, $E°_{298}(M(RX)_p)$ is the formal potential of the complex $M(RX)_p$. Strictly speaking, the various redox potentials in a mixture could undergo shifts due to ligand-exchange equilibria being coupled to the electron-transfer step.[7] The applicability of the additivity rule means that the effect of such coupling on potentials in the present systems is relatively small in practice.

Table I. Mixtures[a] and Formal Potentials[b] of Parent Species

a	$Cu(EtMe)_2$ (−0.78) + $Cu(EtNO_2)_2$ (−0.46)
b	$Cu(EtH)_2$ (−0.75) + $Cu(EtNO_2)_2$ (−0.46)
c	$Cu(EtMe)_2$ (−0.78) + $Cu(PhNO_2)_2$ (−0.37)
d	$Cu(PhOMe)_2$ (−0.66) + $Cu(PhNO_2)_2$ (−0.37)
e	$Co(EtMe)_3$ (−0.56) + $Co(EtNO_2)_3$ (−0.08)
f	$Co(EtH)_3$ (−0.52) + $Co(EtNO_2)_3$ (−0.08)
g	$Fe(EtMe)_3$ (−0.76) + $Fe(PhCl)_3$ (−0.37)
h	$Fe(EtMe)_3$ (−0.76) + $Fe(EtNO_2)_3$ (−0.32)
i	$Fe(EtH)_3$ (−0.71) + $Fe(EtNO_2)_3$ (−0.32)
j	$Fe(EtMe)_3$ (−0.76) + $Fe(PhNO_2)_3$ (−0.15)
k	$Fe(EtMe)_3$ (−0.76) + $Fe(EtCO_2Et)_3$ (−0.46) + $Fe(PhNO_2)_3$ (−0.15)
l	$Fe(EtMe)_3$ (−0.76) + $Fe(PhH)_3$ (−0.46) + $Fe(PhNO_2)_3$ (−0.15)

[a] Solvents (0.1 M in TEAP): dimethylformamide (mixures **a–d**); acetonitrile (mixtures **e–l**). [b] Formal potentials (V vs. SCE) of parent complexes at 298 K are given in parentheses.

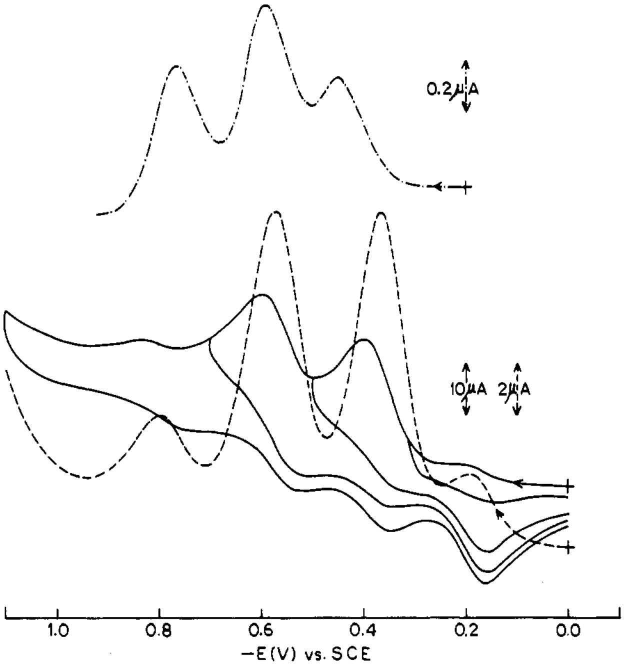

Figure 1. Bottom: Full scan and segmented cyclic voltammogram (—) and differential-pulse voltammogram (---) of an equimolecular mixture of $Fe(EtMe)_3$ + $Fe(PhNO_2)_3$ in acetonitrile at a glassy-carbon electrode. Top: Differential-pulse voltammogram (---) of an equimolecular mixture of $Cu(EtMe)_2$ + $Cu(EtNO_2)_2$ in DMF at a HMDE. Cyclic voltammetry scan rate is 50 mV s^{-1}, differential-pulse voltammetry scan rate is 10 mV s^{-1}, and modulation amplitude is 25 mV.

In the binary mixtures **a–d** and **e–j** three and four responses are respectively observed (Figure 1) as expected. In the ternary mixtures **k** and **l** 10 responses can arise in principle. However, overlap precludes observation of the complete set. For example, in mixture **l** the formal potentials of the pair $Fe(EtMe)_2(PhNO_2)$ and $Fe(EtMe)(PhH)_2$ are the same by the additivity rule. This holds true for two other pairs: $Fe(EtMe)(PhH)(PhNO_2)$, $Fe(PhH)_3$ and $Fe(EtMe)(PhNO_2)_2$, $Fe(PhH)_2(PhNO_2)$ (Tables I and II). Thus, only seven distinct

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Table II. Observed[a–c] and Calculated[d] Formal Potentials of Mixed Complexes

complex	E°_{298}	complex	E°_{298}
$Cu(EtMe)(EtNO_2)$ (1)	−0.60 (−0.62)	$Fe(EtMe)_2(PhNO_2)$ (14)	−0.58 (−0.56)
$Cu(EtH)(EtNO_2)$ (2)	−0.60 (−0.61)	$Fe(EtMe)(EtCO_2Et)_2$ (15)	−0.58 (−0.56)
$Cu(EtMe)(PhNO_2)$ (3)	−0.56 (−0.58)	$Fe(EtMe)(PhH)_2$ (16)	−0.58 (−0.56)
$Cu(PhOMe)(PhNO_2)$ (4)	−0.50 (−0.52)	$Fe(EtMe)(PhCl)_2$ (17)	−0.52 (−0.50)
$Co(EtMe)_2(EtNO_2)$ (5)	−0.41 (−0.40)	$Fe(EtMe)(EtNO_2)_2$ (18)	−0.49 (−0.47)
$Co(EtH)_2(EtNO_2)$ (6)	−0.35 (−0.37)	$Fe(EtMe)(EtCO_2Et)(PhNO_2)$ (19)	−0.47 (−0.46)
$Co(EtMe)(EtNO_2)_2$ (7)	−0.23 (−0.24)	$Fe(EtMe)(PhH)(PhNO_2)$ (20)	−0.48 (−0.46)
$Co(EtH)(EtNO_2)_2$ (8)	−0.21 (−0.23)	$Fe(EtH)(EtNO_2)_2$ (21)	−0.45 (−0.45)
$Fe(EtMe)_2(EtCO_2Et)$ (9)	−0.68 (−0.66)	$Fe(EtMe)(PhNO_2)_2$ (22)	−0.38 (−0.35)
$Fe(EtMe)_2(PhH)$ (10)	−0.67 (−0.66)	$Fe(EtCO_2Et)_2(PhNO_2)$ (23)	−0.38 (−0.36)
$Fe(EtMe)_2(PhCl)$ (11)	−0.64 (−0.63)	$Fe(PhH)_2(PhNO_2)$ (24)	−0.38 (−0.36)
$Fe(EtMe)_2(EtNO_2)$ (12)	−0.64 (−0.61)	$Fe(EtCO_2Et)(PhNO_2)_2$ (25)	−0.24 (−0.25)
$Fe(EtH)_2(EtNO_2)$ (13)	−0.59 (−0.58)	$Fe(PhH)(PhNO_2)_2$ (26)	−0.26 (−0.25)

[a] Solvents (0.1 M in TEAP): dimethylformamide ($Cu(RX)_2$ mixtures); acetonitrile ($Co(RX)_3$ and $Fe(RX)_3$ mixtures). [b] The working electrode is either a HMDE or a glassy-carbon electrode. [c] Scan rates: 50 mV s^{-1} (cyclic voltammetry); 10 mV s^{-1} (differential-pulse voltammetry). [d] Formal potential (V vs. SCE) of mixed complexes are calculated by using the additivity rule (see text) and are given in parentheses.

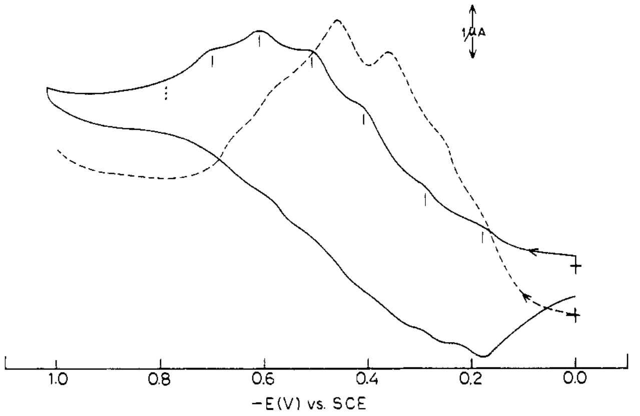

Figure 2. Cyclic voltammogram (—) at a HMDE and differential-pulse voltammogram (---) at a glassy-carbon electrode of an equimolecular mixture of $Fe(EtMe)_3 + Fe(PhH)_3 + Fe(PhNO_2)_3$ in acetonitrile. Scan rates and other parameters are the same as in Figure 1.

responses can arise, of which six[8] are clearly observable (Figure 2).

When X is varied, the formal potentials of the parent species $M(RX)_p$ are known to display[5,6] excellent linear correlation with the weighted Hammett constant ($p\sigma$) of X. The formal potentials of the mixed species fall on the same line when the net substituent constant ($\sum\sigma$) is weighted for the different X substituents. The cases of iron and cobalt are illustrated in Figure 3.

Redistribution Statistics. Since the various ligands differ merely in substituents, the change in entropy rather than enthalpy is likely to control the thermodynamics of redistribution, which should therefore be nearly random in statistics. The concentration ratios of constituent species should then be 1:2:1 (mixtures **a**–**d**) and 1:3:3:1 (mixtures **e**–**j**), where the first and last numbers represent the relative concentration of the two parent species.[9] The differential-pulse voltammetric cathodic peak heights agree qualitatively[10] with the statistical situation (Figure 1).

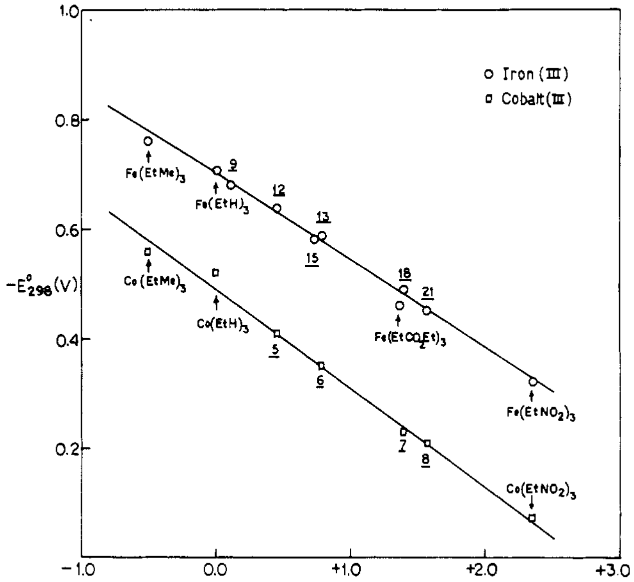

Figure 3. Least-squares plots of E°_{298} vs. $\sum\sigma$ for iron(III) and cobalt(III) mixed complexes. The numbers are the same as in Table II.

In cyclic voltammetric experiments the peak heights in the anodic and cathodic scans are observably different as can be visualized in Figure 1. In particular there is augmented anodic current for the species having highest formal potential. This anomaly, which disappears when the region covering the high-potential response alone is selectively scanned (Figure 1), can arise[11] due to electron cascade from the reduced species

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(8) The unobserved response is the one due to $Fe(EtMe)_3$, expected near −0.8 V. It becomes observable on adding an extra 1 mol of $Fe(EtMe)_3$ to the mixture. The problem of the response at lowest potential becoming relatively inconspicuous also occurs in the binary mixtures. Part of the difficulty no doubt lies in the inherent disadvantage in observing a relatively small response at high elevation on a slope.

(9) In the ternary mixtures **k** and **l** the expected ratio is 1:3:3:6:3:3:1:3:3:1. However, serious overlap of responses (Figure 2) made reliable determination of the ratio impossible.

(10) Quantitative agreement is not expected since the current function is liable to be affected[7] by various equilibria preceding and succeeding electron-transfer steps.

(11) A second factor can be disproportionation reactions such as

$$2\,\mathbf{22}^- + \mathbf{22} \rightleftharpoons Fe(EtMe)_3 + 2Fe(PhNO_2)_3^-$$

$$\mathbf{14}^- + 2\,\mathbf{14} \rightleftharpoons 2Fe(EtMe)_3 + Fe(PhNO_2)_3^-$$

which are thermodynamically favorable.[12] However, lack of augmentation of the cathodic current for $Fe(EtMe)_3$ suggests that in practice such disproportionation reactions may not be very important in the present systems. Authentic examples of such disproportionation of the reduced mixed species in electrochemical experiments occur among copper complexes of 2,2′-bipyridine and 2-(phenylazo)pyridine.[13]

(12) For example, the free energy change in the first reaction in ref 11 is calculated to be ∼−6 kcal from the corresponding changes in the reactions

$$3Fe(EtMe)(PhNO_2)_2 \rightleftharpoons Fe(EtMe)_3 + 2Fe(PhNO_2)_3$$

$$2Fe(PhNO_2)_3 + 2e^- \rightleftharpoons 2Fe(PhNO_2)_3^-$$

$$2Fe(EtMe)(PhNO_2)_2^- \rightleftharpoons 2Fe(EtMe)(PhNO_2)_2 + 2e^-$$

whose equilibrium constants are known from consideration of random statistics or formal potential data (Tables I and II).

formed during the cathodic scan. Thus, $Fe(PhNO_2)_3$ by virtue of its highest formal potential can favorably (in the thermodynamic sense) receive[14] electrons from $Fe(EtMe)_3^-$, $Fe(EtMe)_2(PhNO_2)^-$, and $Fe(EtMe)(PhNO_2)_2^-$. On the other hand $Fe(PhNO_2)_3^-$ has no acceptor available. The effective concentration of $Fe(PhNO_2)_3^-$ available for oxidation at the electrode surface would thus increase, resulting in the observed effect.

Concluding Remarks. Facile ligand redistribution occurs in mixtures of triazene 1-oxide complexes of copper(II), cobalt(III), and iron(III). In ternary mixtures of iron(III) complexes, six closely spaced but clearly observable voltammetric responses occur. Such a system could act like a sponge for reversibly absorbing electrons over the applicable potential range. Whereas fast redistribution is not unexpected in the cases of the high-spin[5] iron(III) and copper(II) complexes, it is somewhat surprising[15] that the stereochemically rigid (meridional, ^{1}H NMR data[16]) low-spin cobalt(III) species also redistribute as readily. The redistribution reactions preclude the possibility of isolating mixed species in pure state.[17]

We are not aware of any other technique outside voltammetry by which the formation of the various mixed complexes could be established with such ease, authenticity, and generality. Virtually all previous voltammetric studies[3,4] on ligand redistribution concern dithiolenes, dithiocarbamates, and related species. To the best of our knowledge, the present work represents the first thorough and systematic report on O,N systems and on the effect of remote substituents (X) in mixed complexes.

Experimental Section

Materials. Complexes of types $Cu(RX)_2$, $Co(RX)_3$, $Fe(RX)_3$, and $Ru(RX)_3$ were synthesized as reported.[5,6] Solvents and supporting electrolyte for electrochemistry were purified as before.[5]

Formation of Mixed Complexes. Equimolar amounts ($\sim 10^{-3}$ M) of the two or three parent complexes together with the supporting electrolyte (tetraethylammonium perchlorate, TEAP) were allowed to equilibrate in the voltammetric vessel at 298 K in dimethylformamide ($Cu(RX)_2$ mixtures) or in acetonitrile ($Co(RX)_3$, $Fe(RX)_3$, and $Ru(RX)_3$ mixtures) for 2 h. Voltammetric examination however showed that redistribution equilibrium is achieved in most cases within the time of mixing. Only in the case of copper(II) species is a larger time needed. The equilibration time of 2 h was chosen to ensure that equilibrium is surely reached.

Electrochemical Measurements. A PAR Model 370-4 electrochemistry system, which includes the 174A polarographic analyzer, 175 universal programmer, and RE 0074 X-Y recorder, was used. The three-electrode measurements were carried out with either a Metrohm E 410 hanging-mercury-drop electrode (HMDE) or a G0021 glassy-carbon electrode, a platinum-wire counterelectrode, and a saturated calomel reference electrode (SCE). The cell was thermostated at 298 K. All measurements were carried out under a dinitrogen atmosphere. The results reported are uncorrected for junction potentials.

The formal potentials $E°_{298}$ were calculated as follows: (i) cyclic voltammetry, the average of the cathodic (E_{pc}) and anodic (E_{pa}) peak potentials; (ii) differential-pulse voltammetry, $E_p = E°_{298} + 0.5\ \Delta E$, where E_p is the peak potential and ΔE is the modulation amplitude. A ΔE value of 25 mV was uniformly used.

The following σ values[5] for para substituents were used: Me, −0.17; H, 0.00; Cl, +0.23; CO_2Et, +0.45; NO_2, +0.78.

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Registry No. $Cu(EtMe)(EtNO_2)$, 93255-38-0; $Cu(EtH)(EtNO_2)$, 93255-39-1; $Cu(EtMe)(PhNO_2)$, 93255-40-4; $Cu(PhOMe)(PhNO_2)$, 93255-41-5; $Co(EtMe)_2(EtNO_2)$, 93255-42-6; $Co(EtH)_2(EtNO_2)$, 93255-43-7; $Co(EtMe)(EtNO_2)_2$, 93255-44-8; $Co(EtH)(EtNO_2)_2$, 93255-45-9; $Fe(EtMe)_2(EtCO_2Et)$, 93255-46-0; $Fe(EtMe)_2(PhH)$, 93255-47-1; $Fe(EtMe)_2(PhCl)$, 93255-48-2; $Fe(EtMe)_2(EtNO_2)$, 93255-49-3; $Fe(EtH)_2(EtNO_2)$, 93255-50-6; $Fe(EtMe)_2(PhNO_2)$, 93255-51-7; $Fe(EtMe)(EtCO_2Et)_2$, 93255-52-8; $Fe(EtMe)(PhH)_2$, 93255-53-9; $Fe(EtMe)(PhCl)_2$, 93255-54-0; $Fe(EtMe)(EtNO_2)_2$, 93255-55-1; $Fe(EtMe)(EtCO_2Et)(PhNO_2)$, 93255-56-2; $Fe(EtMe)(PhH)(PhNO_2)$, 93255-57-3; $Fe(EtH)(EtNO_2)_2$, 93255-58-4; $Fe(EtMe)(PhNO_2)_2$, 93255-59-5; $Fe(EtCO_2Et)_2(PhNO_2)$, 93255-60-8; $Fe(PhH)_2(PhNO_2)$, 93255-61-9; $Fe(EtCO_2Et)(PhNO_2)_2$, 93255-62-0; $Fe(PhH)(PhNO_2)_2$, 93255-63-1; $Cu(EtMe)_2$, 32425-23-3; $Cu(EtH)_2$, 32425-19-7; $Cu(PhOMe)_2$, 14647-29-1; $Cu(EtNO_2)_2$, 79972-14-8; $Cu(PhNO_2)_2$, 79972-17-1; $Co(EtMe)_3$, 79972-06-8; $Co(EtH)_3$, 77188-06-8; $Co(EtNO_2)_3$, 79972-10-4; $Fe(EtMe)_3$, 79971-92-9; $Fe(EtH)_3$, 77188-05-7; $Fe(PhCl)_3$, 79972-02-4; $Fe(EtNO_2)_3$, 79971-96-4; $Fe(PhNO_2)_3$, 79972-04-6; $Fe(EtCO_2Et)_3$, 79971-95-2; $Fe(PhH)_3$, 28660-76-6.

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(14) It is reasonable to assume that the kinetic barrier to electron transfer between the closely related complexes would be small.

(15) The voltammetric solvent (acetonitrile, 0.1 M in TEAP) is however different from the ^{1}H NMR solvent[16] (neat $CDCl_3$).

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(17) Thus, when iron(III) acetate is reacted with 3 mol of an equimolar mixture of the ligands HEtMe and $HPhNO_2$, the crystalline material isolated has a voltammogram identical with that of mixture j.

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Synthesis and Characterization of the Alkoxo-Bridged Chromium(III) Dimer Bis(μ-methoxo)bis[bis(2,2,6,6-tetramethyl-3,5-heptanedionato)chromium(III)]

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The effect of slight structural variations on the magnetic properties of chromium(III) dimers has been studied[2–13] with close attention paid to the impact of changes in the bridging geometry of μ-hydroxo- and bis(μ-hydroxo) chromium(III)

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