Table I

Isomer	Atom	Q_{AA}	ΣQ_{AB}	$\sigma^{(d)}$	δ Obsd[a]	δ Calcd[b]
o (1,2)	B3	1.211	0.123	187.8	15.2	16.7
	B4	1.250	0.128	188.8	13.9	12.5
	B8	1.300	0.131	190.0	9.9	7.4
	B9	1.300	0.136	190.0	2.7	6.8
m (1,7)	B2	1.197	0.123	187.6	17.3	18.2
	B4	1.251	0.127	188.8	13.6	12.5
	B5	1.252	0.131	188.8	11.0	11.9
	B9	1.301	0.132	190.0	7.0	7.2
p (1,12)	B2	1.251	0.127	188.8	15.2	12.5

[a] See ref 7. The chemical shifts are expressed in parts per million from boron trifluoride etherate. [b] These values are calculated using the equation of the least-squares line given in Figure 1: $\delta^{calcd} = \sigma^{(d)} - 12.4 - 118.9(Q_{AA} + \Sigma Q_{AB})$.

will probably dominate the chemical shifts of other boron compounds.

Acknowledgment. We wish to thank the Office of Naval Research for support of this research.

F. P. Boer
The Dow Chemical Company, Eastern Research Laboratories
Wayland, Massachusetts 01778

R. A. Hegstrom, M. D. Newton, J. A. Potenza, W. N. Lipscomb
Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

Received August 29, 1966

Excited State p*K*'s. IV. Tautomeric Equilibria

Sir:

It has been shown[1] that the equilibrium constants for acid–base reactions in electronically excited states can be obtained, if only approximately, from the electronic absorption spectra of the conjugate acid–base pair by use of the Förster cycle. In principle, the method should be applicable to any type of equilibrium constants. Of particular interest may be tautomeric equilibria which, when occurring in polar media, may be expressed as a combination of several acid–base reactions, and which may be established fast enough to occur in excited singlet states. In connection with our studies of the basic properties of amino-substituted azo and azoxy compounds,[2] we have observed some rather extreme cases of shifts of tautomeric equilibria between ground and excited states.

Table I

Compd	pK_1	pK_1*	pK_2	pK_2*	pK_3	pK_3*	pK_4	pK_4*	pK_T	pK_T*
p-Dimethylaminoazobenzene	4.42[a]	−9.64[e]	5.27[f]	7.84[e]	−4.43[h]	10.76[e]	−5.28[f]	−15.59[e]	−0.85[h]	−26.3[e]
p-Dimethylaminoazobenzene N-oxide	−4.91[b]	9.84[f]	4.11[g]	4.11[e]	4.37[f]	4.37[e]	−4.65[g]	10.1[e]	−9.02[f]	5.7[f]
β-Dimethylaminoazoxybenzene	−5[c]	5.6[f]	2.62[g]	−15.58[e]	−0.4[f]	−18.5[j]	−8.02[g]	2.68[e]	−7.6[f]	20[f]
β-Dimethylaminoazoxybenzene N-oxide	−8.59[d]	1.22[f]	3.71[g]	3.71[e]	3.89[f]	3.89[k]	−8.41[g]	1.39[e]	−12[f]	−2[f]
2,3-Aminonaphthol	11.2[a]	6.7[a]	6.0[f]	0.3[e]	2.8[i]	−8.2[e]	8.0[c]	−1.8[a]	5.2[f]	6.4[f]

[a] Calculated from the Hammett equation using parameters from H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953). [b] Presumed equal to the p*K* of *p*-phenylazo-N,N,N-trimethylanilinium ion.[2a] [c] Calculated from the Hammett equation using parameters from ref 2c. [d] Calculated from the Hammett equation assuming $\sigma_{NO(CH_3)_2} = \sigma_{N(CH_3)_3}$. [e] Calculated from the Förster cycle. [f] Calculated from the relationships within the equation scheme. [g] Experimental, Ellerhorst and Jaffé, unpublished work. [h] Experimental.[2a] [i] Experimental.[4] [j] Constant Δp*K* assumed for equilibria 2 and 3. [k] Assumed Δp*K* = 0.

If we examine the equilibrium diagram for the possible equilibria in the first two protonations of a dibasic acid, we arrive at the following scheme in which BH^+ and $B'H^+$ are two tautomeric first conjugate acids of the base B which differ only in the position of attachment of the proton.[3] The equilibrium between BH^+ and $B'H^+$ is defined by the equilibrium constant $K_T = [BH^+]/[B'H^+] = K_2/K_1 = K_3/K_4$.

$$\begin{tikzcd}
& B \arrow[dl, shift left, "K_1"'] \arrow[dr, shift left, "K_2"] & \\
BH^+ \arrow[ur, shift left] \arrow[rr, shift left, "K_T"] \arrow[dr, shift left, "K_3"'] & & B'H^+ \arrow[ll, shift left] \arrow[ul, shift left] \arrow[dl, shift left] \\
& BH^{2+} \arrow[ul, shift left] \arrow[ur, shift left, "K_4"'] &
\end{tikzcd}$$

We have recently observed a number of such equilibria in which the equilibrium constants undergo tremendous changes upon excitation. Thus, the equilibrium between the azonium and ammonium forms of dimethylaminoazobenzene (DMAB) first conjugate acid, in which both forms are present in measurable quantities ($K_T = 7.15$), shifts, upon excitation, in the direction of the pure azonium form to the complete exclusion of the ammonium form ($K_T^* \approx 10^{26}$). Similarly, in the first conjugate acid of the N-oxide of DMAB, the equilibrium shifts from a pure N-hydroxy-DMAB cation ($K_T \approx 10^6$) in the ground state to a pure azonium cation ($K_T^* \approx 10^{-9}$) in the singlet excited state. In dimethylaminoazoxybenzene a similar change from an ammonium to an azonium form occurs ($K_T \approx 10^8$; $K_T^* \approx 10^{-21}$). In the amino N-oxide of the latter compound, the change in K_T is still quite large, but the equilibrium position is not reversed; the N-hydroxyammonium salt is stable in ground and excited states. However K_T^* is quite small, and it seems feasible that the hydroxyazonium form may be observable. Finally, a similar analysis of the aminonaphthols[4] suggests that K_T changes are much smaller, and no reversal of stable forms occurs; *i.e.*, the neutral form rather than the zwitterion is the stable form in both ground and excited states.

The data here presented are subject to a great deal of uncertainty. First, the Förster cycle is used throughout, and is known to yield only approximate results.[1b,5]

---

[1] *Cf.*, *e.g.* (a) H. H. Jaffé, D. L. Beveridge, and H. L. Jones, *J. Am. Chem. Soc.*, **86**, 2932 (1964); (b) H. H. Jaffé and H. L. Jones, *J. Org. Chem.*, **30**, 964 (1965).

[2] (a) S. J. Yeh and H. H. Jaffé, *J. Am. Chem. Soc.*, **81**, 3283 (1959); (b) M. Isaks and H. H. Jaffé, *ibid.*, **86**, 2209 (1964); (c) C. S. Hahn and H. H. Jaffé, *ibid.*, **84**, 949 (1962).

[3] Note that throughout basicities of bases are expressed as pK_a of the conjugate acid.

[4] D. W. Ellis and L. B. Rogers, *Spectrochim. Acta*, **20**, 1709 (1964).

[5] (a) E. L. Wehry and L. B. Rogers, *ibid.*, **21**, 1976 (1965); (b) J. C. Haycook, S. F. Mason, and B. E. Smith, *J. Chem. Soc.*, 4897 (1963).

Second, many p*K*'s are estimated on the basis of the Hammett equation or on the basis of crude approximation of substituent effects, as explained in the footnotes to Table I. However, the effects observed are so large that uncertainties of even a power of ten in K_T appear insignificant. Thus, we can conclude that, at least occasionally, we may expect to see tautomeric equilibria shift completely from one side to the other upon electronic excitation. This fact may be of considerable importance in considerations of the mechanism of photochemical reactions, because the reacting species may be a tautomer not occurring in the ground state.

---

[6] U. S. Public Health Service Fellow, 1963–1965.

[7] National Aeronautics and Space Administration Trainee, 1964–1966.

R. H. Ellerhorst,[6] H. H. Jaffé, Albert L. Miller[7]
Department of Chemistry, University of Cincinnati
Cincinnati, Ohio 45221

Received October 6, 1966

Inner-Sphere Mechanisms for the Reduction of Cobalt(III) Complexes by Iron(II)[1]

Sir:

Since the discovery[2] of the bridged activated complex in the $Co(NH_3)_5Cl^{2+}$–Cr^{2+} reaction, many electron-transfer reactions have been studied in order to determine whether inner- or outer-sphere mechanisms obtain.[3] For reducing agents such as chromium(II)[4] and pentacyanocobaltate(II),[5] the product criterion of mechanism is applicable.[3] For other reducing agents (iron(II), vanadium(II), europium(II)),[6–9] however, the primary reaction products cannot, in general, be identified since the rates of substitution in the coordination spheres of the oxidation products are usually rapid compared to the rates of the oxidation–reduction reactions.[10,11]

In spite of the lability of iron(III) complexes, we have found that the reductions of $Co(C_2O_4)_3^{3-}$, $Co(H{\cdot}EDTA)Cl^-$, $Co(en)_2(OH_2)Cl^{2+}$, $Co(NH_3)_3(OH_2)_2Cl^{2+}$, $Co(NH_3)_3(OH_2)_2N_3^{2+}$, and $Co(NH_3)_3(OH_2)C_2O_4^+$ by iron(II) were sufficiently rapid so that the primary iron(III) products of these reactions could be identified.[12] The identification was performed by determining the spectrum of the iron(III) product and by observing its rate of formation and decay. These measurements were made with the rapid-flow apparatus described previously.[13]

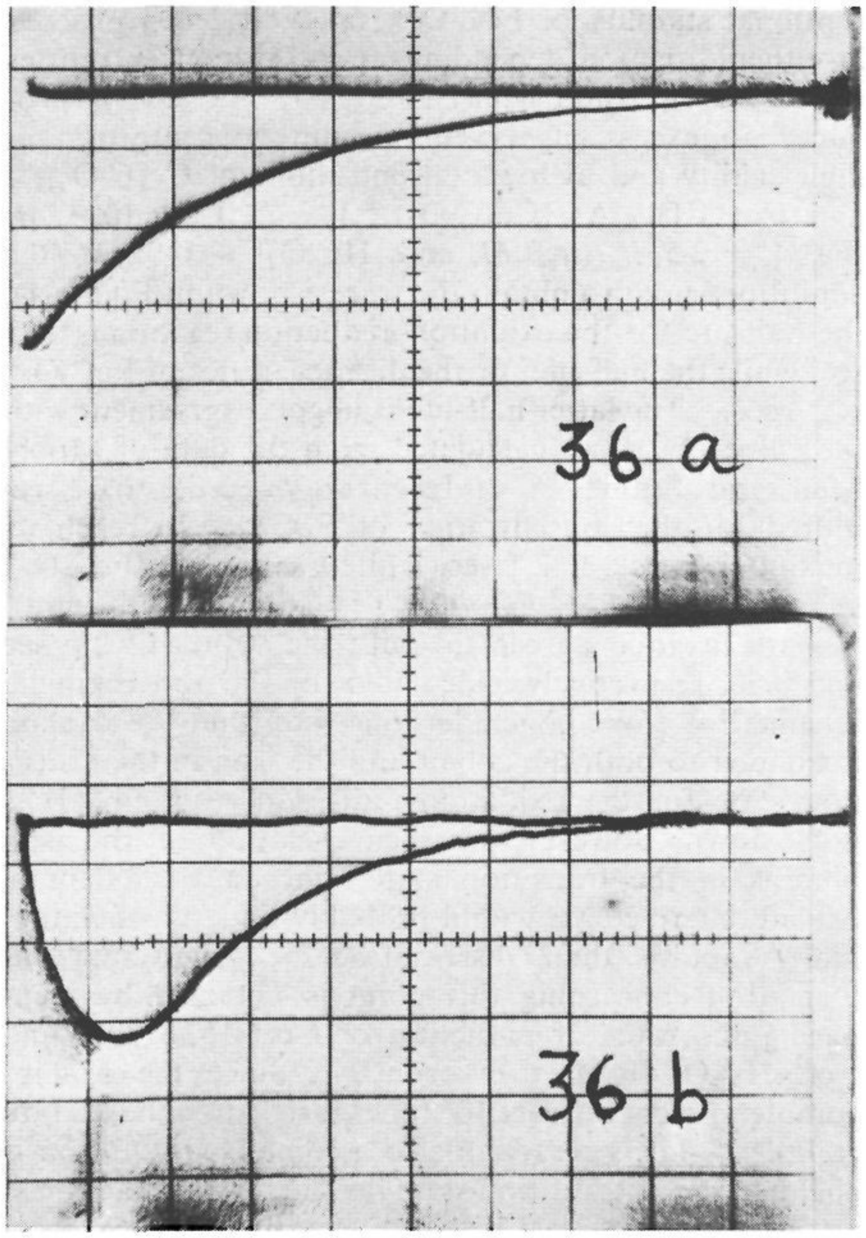

Figure 1. Transmittance *vs.* time curves for the $Co(C_2O_4)_3^{3-}$–Fe^{2+} reaction at 25°. $[Co(C_2O_4)_3^{3-}] = 1.0 \times 10^{-3}$ *M*, $[Fe^{2+}] = 2.5 \times 10^{-2}$ *M*, $[HClO_4] = 0.92$ *M*, ionic strength = 1.0 *M*. Upper curve (36a) shows the disappearance of $Co(C_2O_4)_3^{3-}$: wavelength, 600 mμ; abscissa scale, 500 msec per major division. Lower curve (36b) shows the formation and disappearance of the intermediate $FeC_2O_4^+$: wavelength, 310 mμ; abscissa scale, 2 sec per major division.

The $Co(C_2O_4)_3^{3-}$–Fe^{2+} Reaction. This reaction proceeds in two stages.

$$Co(C_2O_4)_3^{3-} + Fe^{2+} \longrightarrow FeC_2O_4^+ + Co^{2+} + 2C_2O_4^{2-} \quad (1)$$

$$FeC_2O_4^+ + 2H^+ \rightleftharpoons Fe^{3+} + H_2C_2O_4 \quad (2)$$

By using different wavelengths, both the disappearance of $Co(C_2O_4)_3^{3-}$ and the formation and subsequent decay of $FeC_2O_4^+$ were observed. The disappearance of the cobalt(III) complex was followed at 600 mμ, an absorption maximum of $Co(C_2O_4)_3^{3-}$ and a region where none of the other reactants or products absorb significantly. The rate constant for the oxidation–reduction reaction is $(3.3 \pm 0.1) \times 10^1$ M^{-1} sec^{-1} at 25.0° and ionic strength 1.0 *M*.[14] The formation and disappearance of $FeC_2O_4^+$ was followed at 310 mμ. As shown in the lower curve of Figure 1, a rapid decrease in transmittance associated with the oxidation–reduction step is followed by an increase in transmittance corresponding to the disappearance of the $FeC_2O_4^+$ formed in the first step. Because of the ex-

---

[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] H. Taube, H. Myers, and R. L. Rich, *J. Am. Chem. Soc.*, **75,** 4118 (1953).

[3] For a recent review of this subject, see N. Sutin, *Ann. Rev. Phys. Chem.*, **17,** 119 (1966).

[4] H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1,** 1 (1959).

[5] J. P. Candlin, J. Halpern, and S. Nakamura, *J. Am. Chem. Soc.*, **85,** 2517 (1963).

[6] A. M. Zwickel and H. Taube, *ibid.*, **83,** 793 (1961).

[7] J. P. Candlin, J. Halpern, and D. L. Trimm, *ibid.*, **86,** 1019 (1964).

[8] J. H. Espenson, *Inorg. Chem.*, **4,** 121 (1965).

[9] H. Diebler and H. Taube, *ibid.*, **4,** 1029 (1965).

[10] It must be noted, however, that $FeCl^{2+}$ has been identified as the primary product of the $CoCl^{2+}$–Fe^{2+} reaction.[11]

[11] T. J. Conocchioli, G. H. Nancollas, and N. Sutin, *J. Am. Chem. Soc.*, **86,** 1453 (1964).

[12] This criterion appears to be applicable to the $Co(NH_3)_5C_2O_4H^{2+}$–Fe^{2+} reaction. Calculations indicate that at low acid concentration the rate of this reaction[8] becomes comparable to the rate of dissociation of $FeC_2O_4^+$.[15] We are planning to study this reaction in detail.

[13] G. Dulz and N. Sutin, *Inorg. Chem.*, **2,** 917 (1963).

[14] The rate constant for reaction 1 is 1.15×10^3 M^{-1} sec^{-1} at 20° and zero ionic strength: J. Barrett and J. H. Baxendale, *Trans. Faraday Soc.*, **52,** 210 (1956). The lower rate constant determined in the present work is consistent with the effect of ionic strength on the reaction rate.