Contribution from the Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia 13, Bulgaria

Redox Reactions of Metal Ions. II. Correlations of Reagent Electronic Structure Parameters with Reaction Rates

G. St. Nikolov

Received January 11, 1971

Correlations between activation energy and basicity constants of the reductants are found for a number of redox reactions proceeding with metal ions as oxidants. Two types of correlation equations are found giving a possibility for discerning between weak and strong type of interaction of the reactants in the activation state. The activation energy is found to depend also on the energy of the reductant for a series of reactions with one and the same oxidant.

Introduction

In the first Part of this series[1] it was shown that in many redox reactions of vanadium(V) the charge on the reactive site of the reductant markedly affects the energy of activation. The correlation between the activation energy (ΔE*) and basicity constants of the reductants (log β) for the redox reactions of vanadium(V) was explained in terms of the close analogy between nucleophilicity and redox behaviour of the compounds oxidized by vanadium(V).[1] It might be therefore of interest to check whether this correlation observed for vanadium(V) as oxidant is, in general, valid for other oxidants.

In the present paper we present the results for cobalt(III) and cerium(IV) redox reactions.

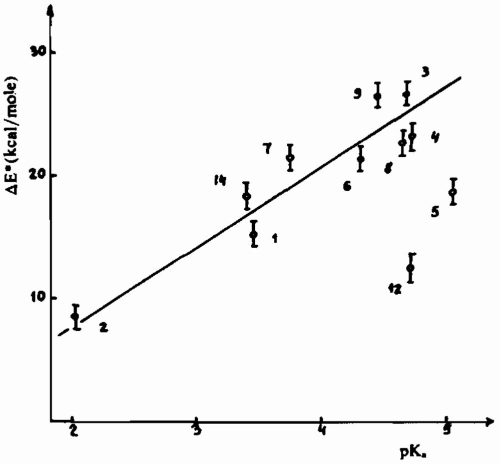

Figure 1. The dependence of ΔE* on pK_a for cobalt(III) oxidation reactions. Compounds numbered as in Table I.

Results and Discussion

The relevant experimental data collected from literature sources are presented in Tables I and II. Taking the acid dissociation constants (note that log $\beta = pK_a$) from,[2,3] the plots $\Delta E^*/pK_a$ are obtained (Fi-

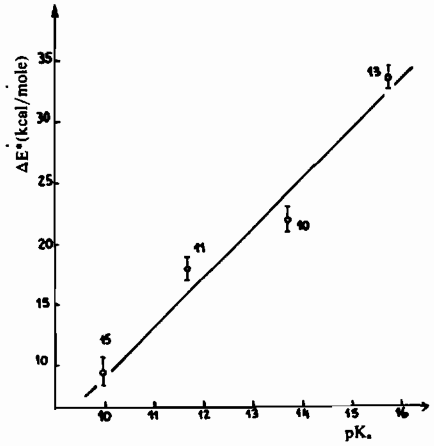

Figure 2. The dependence of ΔE* on pK_a of substrate for cobalt(III) reactions. Compounds numbered as in Table I. $(\Delta E^* \pm 2) = 4.05 pK_a - 30.6$(kcal/mole).

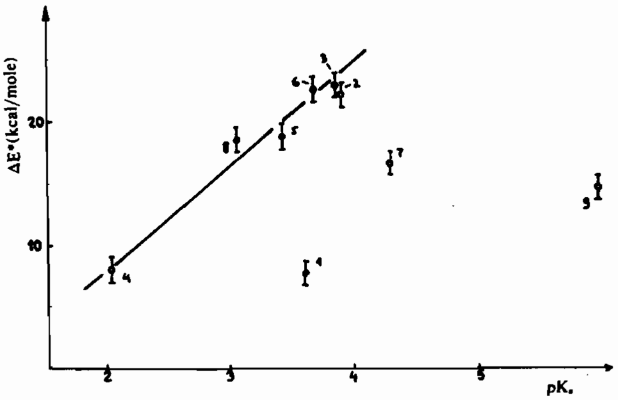

Figure 3. The dependence of ΔE* on pK_a of substrate for cerium(IV) redox reactions. Compounds numbered as in Table II.

---

(1) G. St. Nikolov and K.B. Yatsimirskii, *Theoret. Exp. Chem.*, (USSR) 5, 773 (1969) and refs. therein.

(2) *Stability Constants*, Eds. L.G. Sillen and A.E. Martell, *Chem. Soc. Special Publ.*, London (1964).

(3) A. Albert and E. Sergeant, *Ionization Constants of Acids and Bases*, Russ. Transl., Publ. House « Khimia », Moscow, 1964.

Table I. Energy and entropy of activation for redox reactions of cobalt(III).

No	Compound oxidized	ΔE^* kcal/mole	ΔS^* e.u.	Ref.	pK_a [2,3]	$-W_{HOMO}$[4] (eV)	Remarks
1.	Malic acid	15.3	—	[5]	3.46	11.73	*a*
2.	Thiourea	8.6	—29	[6]	2.03	—	*b,c*
3.	Propionic acid	26.7	21.4	[7,8]	4.87	—	*a,c*
4.	iso-Butyric acid	22.6	16.1	[7,8]	4.86	—	*a,c*
5.	Pivalic acid	18.7	4.1	[7,8]	5.05	—	*a,c*
6.	Phenylacetic acid	21.4	13.1	[7,8]	4.31	—	*a,c*
7.	Formic acid	21.7(27)	21.1	[9]	3.75	11.79	*a*
8.	Crotonic acid	23.6	13.1	[7]	4.69	—	*a,c*
9.	Cinnamic acid	26.5	32.6	[7]	4.44	—	*a,c*
10.	Formaldehyde	22.0	20.0	[10]	13.7	12.37	*a*
11.	H_2O_2	18.0	55	[11,12]	11.65	12.14	*a*
12.	HN_3	12.6	— 3.6	[12]	4.72	11.30	*a,c*
13.	H_2O	33.6(39.6)	—	[13,14]	15.74	14.17	*a,c*
14.	HNO_2	18.3	9	[15]	3.4	12.70	—
15.	Hydroquinone	9.7(18.2)	18	[15,16]	9.96	7.35	—

[a] rapid complex formation; [b] slow complex formation; [c] complex detected in the reaction course. pK_a values are for 25°C and zero ionic strength with the exception of thiourea ($\mu = 0.01$), formaldehyde (18°C) and hydroquinone (18°C).

Table II. Energy and entropy of activation fro redox reactions of cerium(IV).

No	Compound Oxidized	ΔE^* kcal/mole	ΔS^* e.u.	Remarks	Ref.	pK_a [2,5]	$-W_{HOMO}$[4] (eV)
1	Thioglycollic acid	7.9	—23	*a,c*	[17]	3.60	—
2.	Lactic acid	22.5	3	*a*	[18]	3.86	—
3.	Glycollic acid	23.0	12	*a,c,d*	[19,20]	3.83	—
4.	Thiourea	8.0	—33	*a,c*	[21]	2.03	—
5.	Mandelic acid	18.9	— 0.3	*a,c,d*	[22]	3.41	—
6.	α-OH-butyric acid	22.8	45	*a,c,d*	[22]	3.65	—
7.	Oxalic acid	16.9	—	*a,c*	[23]	1,25;4,27	12.14
8.	Benzilic acid	18.7	7	*a,d*	[24]	3.04	—
9.	NH_2OH	14.8	— 7	*a,c*	[25]	5.96	14.19

[a] rapid complex formation; [c] complex detected in the reaction course; [d] rate of reaction dependent on H_2SO_4 concentration. pK_a values are for 25°C and zero ionic strength with the exception of thiourea ($\mu = 0.01$), and α-OH-bytiric acid (30°C and 0,1 *M*).

Table III. Least-square parameters of the equation: $\Delta E^* = b.pK_a + a$.

Oxidant	b	a kcal/mole	r	Type of interaction	Ref.
V^V	— 3.27	29.1	— 0.9987	weak	[1]
Co^{III}	+ 5.76	— 2.38	+ 0.9271	strong	This work
Ce^{IV}	+ 8.02	— 7.55	+ 0.9773	strong	This work

gures 1, 2, and 3). ΔE^* values are accurate to ±1 kcal/mole and pK_a values to ±0.01. The experimental points are drawn with the corresponding spreading in error. The least-square correlation parameters are given in Table III.

The reagents from Figure 2 observe the general trend (Figure 1), both ΔE^* and pK_a are increased from left to right. The reason for the different slopes of the curves in Figures 1 and 2 is probably some differences in structure of the compounds. The deviation of pivalic acid and HN_3 for cobalt(III) and thioglycollic acid, oxalic acid and NH_2OH for cerium(IV) reactions however is not clear.

The positive slope of the correlation equations for cobalt(III) and cerium(IV) redox reactions could be tentatively explained as follows. It is known that the stability constants in some cases are related to the

---

(4) S. Fraga, Technical Reports TC 6906, 6917 (1969); 7001 (1970), Univ. Alberta, Department of Chemistry, Canada.
(5) J. Hill and A. McAurey, *J. Chem. Soc.* (A), 1169 (1968).
(6) A. McAuley and U.B. Gomwalk, *J. Chem. Soc.* (A), 977 (1969).
(7) W.A. Waters, *Discuss. Faraday Soc., 46,* 158 (1968), and refs. therein.
(8) A.A. Clifford and W.A. Waters, *J. Chem. Soc.*, 2796 (1965).
(9) C.E.H. Bawn and A.G. White, *J. Chem. Soc.*, 339 (1951).
(10) G. Hargreaves and L.H. Sutcliffe, *Trans. Faraday Soc., 51,* 786 (1955).
(11) J.H. Baxendale, *Adv. Catalysis and Related Subjects, 5,* 31 (1952).
(12) C.F. Wells, *Discuss. Faraday Soc., 46,* 195 (1968).
(13) C.E.H. Bawn and A.G. White, *J. Chem. Soc.*, 331 (1951).
(14) M. Anbar and I. Pecht, *J. Am. Chem. Soc., 89,* 2553 (1967).
(15) G. Davies and K.O. Watkins, *J. Phys. Chem., 74,* 3389 (1970).
(16) C.F. Wells and L.V. Kuritsyn, *J. Chem. Soc.* (A), 1372 (1970).
(17) J. Hill and A. McAuley, *J. Chem. Soc.* (A), 156 (1968).
(18) K.P. Bhargava, R. Shanker, and J,N. Joshi, *J. Sci. Ind. Res. India, 216,* 373 (1962).
(19) A. McAuley, *J. Chem. Soc.*, 4054 (1965).
(20) G.V. Bakore, R. Dayal, and P. Nath, *Z. phys. Chem.* (*Leipzig*), *227,* 19 (1964).
(21) U.D. Gomwalk and A. McAurey, *J. Chem. Soc.* (A), 2948 (1968).
(22) A. McAuley and C.H. Brubaker Jr., *J. Chem. Soc.* (A), 960 (1966).
(23) V.H. Dodson and A.H. Black, *J. Am. Chem. Soc., 79,* 3657 (1957).
(24) V.K. Grover and Y.K. Gupta, *J. Inorg. Nucl. Chem., 31,* 1403 (1969).
(25) W.A. Waters and I.R. Wilson, *J. Chem. Soc.* (A), 534 (1966).

basicity constants of the ligands.[26] This relation is expected to hold for similar in structure ligands, as in the case of cerium(IV) reactions (Figure 3 with the exception of thiourea). Complex formation between the reactants is bound to lower the energy of the reacting system. For many reactions of cobalt(III) and cerium(IV) complex formation with the compounds to be oxidized has been detected experimentally (see references to Tables I and II). Unfortunately the stability constants of these complexes were not determined.

However the activated complex usually differs greatly from the initial complex.[27] The energy of reorganization of the initial complex so that the activated state could be formed[28] should be added to the overall activation energy of the reaction. Assuming considerable difference between the initial and activated complexes it is evident that the more stable the initial complex the higher the energy of reorganization to put the reactants in the activated state required for the electron transfer reaction.

The above reasoning could be checked in two different ways. For weak interaction (negligible overlap between orbitals of the reactants in the activated state) Marcus' theory[29] predicts a slope of 1/2 for the plot $\Delta G^*/\Delta G^\circ$ (ΔG^*, free energy of activation; ΔG°, free energy of electron transfer calculated from the oxidation potentials). Taking the oxidation potentials from,[30,31] ΔG° was calculated, and ΔG^* was found from data of Tables I and II, and from Table VIII of reference.[1] The plot $\Delta G^*/\Delta G^\circ$ is shown in Figure 4. As seen most of the reagents oxidized by vanadium(V) lie near to the line with the theoretically predicted slope of 1/2 for weak interaction. The points for cobalt(III) and cerium(IV) lie below that line indicating strong interaction (considerable overlap between orbitals of the reactants). Thus the plot $\Delta G^*/\Delta G^\circ$ seems to support the division made on the basis of the different slopes for the curves $\Delta E^*/pK_a$, and designated in the last column of Table III.

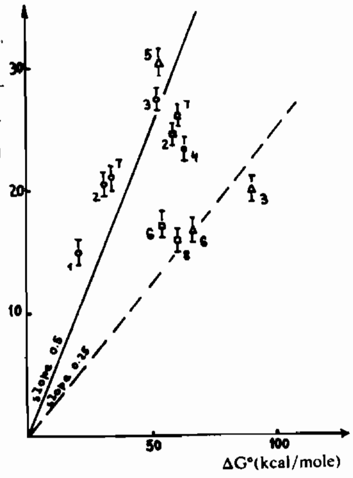

Figure 4. The dependence of the free energy of activation (ΔG^*) on the free energy of electron transfer (ΔG°). (1) Iodide; (2) Glycollic acid; (3) Formic acid; (4) Oxalic acid; (5) Water; (6) Thiourea; (7) Lactic acid (8) Thioglycollic acid; o - for vanadium(V); Δ - for cobalt(III); □ - for cerium(IV) redox reactions.

The second check is more straightforward. In a theretical study on autooxidation of phenolic compounds, Eyring *et al.*[32] have found that the higher the energy of the highest occupied molecular orbital (HOMO) of phenols the more easily they are oxidized, the trend being probably related to the energy gain resulting on electron transfer. Following the arguments of these authors we have tried to correlate ΔE^*

Table IV. Least-square correlation parameters for the equation $\Delta E^* = b.W_{HOMO} + a$ (eV).

Oxidant	b	a (eV/mole)	r
Vanadium(V)	— 0.134	— 0.585	— 0.9988
Cobalt(III)	— 0.283	— 2.606	— 0.9034

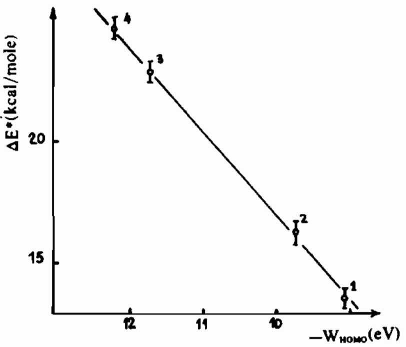

Figure 5. The dependence of ΔE^* on the energy of the highest occupied molecular orbital (W_{HOMO}) of compounds oxidized by vanadium(V). ΔE^* data taken from [1], and W_{HOMO} - from [4]. (1) Aniline; (2) Phenol; (3) Formic acid; (4) Oxalic acid.

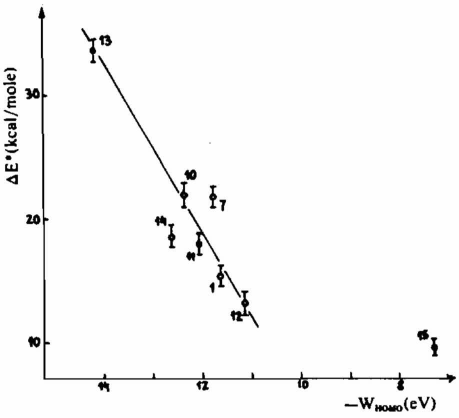

Figure 6. The dependence of ΔE^* on the energy of the highest occupied molecular orbital (W_{HOMO}) of compounds oxidized by cobalt(III). Compounds numbered as in Table I.

---

(26) F.S. Rossotti, Chapter 1 in *Modern Coordination Chemistry*, Eds. R.G. Williams and J. Lewis, Interscience Publ. (1960).

(27) K.B. Yatsimirskii, *Theoret. Exp. Chem.* (USSR), *1*, 343 (1965).

(28) B.J. Zwolinski, R. Marcus, and H. Eyring, *Chem. Rev.*, *55*, 157 (1955).

(29) R.A. Marcus, *J. Chem. Phys.*, *24*, 966 (1956); *idem*, *J. Phys. Chem.*, *67*, 853 (1963).

(30) W.M. Latimer, *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions*, New York, Prentice Hall, 1952.

(31) W.M. Clark, *Oxidation Reduction Potentials of Organic Systems*, Bailliere, Tindall and Co., London (1960).

(32) T. Fueno, T. Ree and H. Eyring, *J. Phys. Chem.*, *63*, 1940 (1959).

with the energy of HOMO of substances oxidized by vanadium(V) and cobalt(III). ΔE* values were taken from Tables I and II as well as from Table VIII of,[1] and the energy of HOMO from the Technical Reports of Fraga *et al.*[4] The plots obtained are shown in Figures 5 and 6 and the least-square parameters are collected in Table IV.

The slopes of the two curves are different. The more than double increase in slope for cobalt(III) reactions as compared with vanadium(V) reactions supports the idea that the redox reactions of cobalt(III) proceed via strong interaction mechanisms (stronger dependence on the energy of HOMO), whereas for the redox reactions of vanadium(V) the electrostatic interaction in the activated state should be predominant.[1]

Another point worth mentioning is the nearly constant ratio of ΔE* for two different oxidants and one and the same reductant; the ratio ΔE*(Ce)/ΔE*(V) is 1.37 for lactic, glycollic and mandelic acids, the only exception being oxalic acid. This ratio is very close to the ratio of the oxidation potentials of the oxidants (1.44/1.00), hence proportionality between ΔE* and oxidation potentials may exist. This fact is rather surprising since linear relations are usually obtained with free energies and not with enthalpies or activation energies.[33] This proportionality may be tentatively explained on the assumption of stronger dependence of ΔE* on the electronic structure parameters of the metal ion and weaker dependence on the electronic structure of the reductants. Indeed the small values for the slopes of the $\Delta E^*/W_{HOMO}$ lines (Table IV) seem to support this assumption.

(33) J.O. Edwards, *Inorganic Reaction Mechanisms*, W.A. Benjamin, New York, Chapter 3 (1965).