

on the phosphate by OH^- . Therefore, we anticipated that the presence of one or more phosphates at the 5'-end of the triadenylates would decrease the rate of metal-catalyzed depolymerization, since the terminal phosphates would be more accessible than the internal phosphates and the metals would bind to the terminal phosphates rather than to the internal ones. A likely explanation as to why the oligoadenylates phosphorylated at the 5'-end are actually more susceptible to depolymerization by Pb^{2+} is that the agent that actually attacks the phosphodiester bonds is an ionized molecule of water in the hydration shell of the plumbous ion and that when Pb^{2+} is bound to the terminal 5'-phosphate the ribose residue positions the attacking water of hydration directly at one of the internal phosphodiester bonds.

We examined the products of Pb^{2+} -catalyzed degradation of ApApA, and we did not observe ApAp among the products. All of the other possible products, 2'- and 3'Ap, ApA, and adenosine were detected on the HPLC chromatogram. A likely explanation for the absence of ApAp is that phosphate at the 3'-end also makes the internal phosphodiester bond more susceptible to Pb^{2+} , and when ApAp was formed, it was rapidly converted to Ap.

When the molecular mechanism by which heavy metals exert their toxicity is explained, textbooks assume that the actions of the metals are identical. However, the fact that Pb^{2+} is 50 times more potent at inhibiting globin synthesis in reticulocytes than other heavy metals,¹⁸ indicates that this may not be correct. In explaining the toxicity of metals, the ability of Pb^{2+} to depolymerize RNA is usually ignored but this mechanism may be more important than interactions between Pb^{2+} and proteins.^{6,7} This is indicated both from evidence showing that the ability of mRNA's to program ribosomes is destroyed in the presence of Pb^{2+} at μmol concentrations⁶ and studies by Werner et al. showing that there are particular phosphodiester bonds in an RNA molecule that are exquisitely susceptible to Pb^{2+} -catalyzed cleavage.⁸

Our data on comparing the effects of Nd^{3+} , Fe^{3+} , and Pb^{2+} on 5'-phosphorylated and unphosphorylated oligoadenylates showed that Nd^{3+} differed from the other metals in that the presence of a 5'-phosphate did not increase the susceptibility of the oligoadenylate to Nd^{3+} . Clearly Nd^{3+} must act differently than the other metals in catalyzing the depolymerization of oligonucleotides.

The metal-catalyzed cleavage of phosphodiester bonds in oligoadenylates differs from that in polynucleotides, e.g. ferric salts degraded tri A and tri I, but had little effect on poly A or tRNA. It is unlikely that chelation of the metals to the amino group at the 6-position of adenine plays a role in binding the metal since the 2',5- and 3',5-triinosinates were also degraded by Fe^{3+} . However, chelation at N7 cannot be ruled out. It would be of

interest to determine if trinucleotides of 7-deazaadenine would be depolymerized by ferric salts.

The ability of Fe^{3+} to degrade the trimers is remarkable in that it proceeds by heterogeneous catalysis between the oligonucleotides in aqueous solution and a solid catalyst. This reaction should be reversible since cyclic 2',3'-AMP is an intermediate, and it might be an example of prebiotic synthesis of polyribonucleotides. Deposits of ferric salts are not ordinarily found in vivo, but they do occur in patients who are hypertransfused to treat hematologic dyscrasias such as thalassemia.¹⁹ Deposits of Fe^{3+} salts are also found in patients (usually children) who accidentally ingest iron pills and in patients with hemochromatosis. Since 2',5'-oligoadenylates may be involved with the control of cell growth and macromolecule synthesis^{20,21} as well as in the interferon response, it is possible that iron overload may exert metabolic effects that were not previously suspected.

In the experiments carried out in this study, the metals were present in the 0.1-1.0 mM range. These concentrations exceed the lethal concentrations of most of the metals, and it would be premature to construe that the interferon-induced response is compromised by these metals in vivo. The effect of Pb^{2+} and the other metals that degrade the oligoadenylates on the interferon response must be carried out either in vivo or with tissue culture cells. These studies are in progress. In our previous work on the degradation of RNA by Pb^{2+} we could not detect any effect of Pb^{2+} in the μM range by chemical means, either.⁵ However, deleterious effects were readily detected when a biochemical assay for mRNA that had been exposed to Pb^{2+} was used.⁶

Acknowledgment. This work was supported in part by NIH Grants ES01323 and HD14062. We are grateful to Dr. Robert Suhadolnick of the Temple University School of Medicine for providing (2',5')IpIpI.

Registry No. (2',5')ApApA, 70062-83-8; (3',5')ApApA, 917-44-2; (2',5')pppApApA, 65954-93-0; (2',5')pApApA, 61172-40-5; (3',5')IpIpI, 33403-48-4; (2',5')IpIpI, 84651-06-9; 2'-AMP, 130-49-4; 3'-AMP, 84-21-9; ApA, 2391-46-0; A, 58-61-7; (2',3')cAMP, 634-01-5; poly(A), 24937-83-5; Ba, 7440-39-3; Be, 7440-41-7; Ca, 7440-70-2; Cd, 7440-43-9; Co, 7440-48-4; Cu, 7440-50-8; Hg, 7439-97-6; Mg, 7439-95-4; Mn, 7439-96-5; Ni, 7440-02-0; Pb, 7439-92-1; Sr, 7440-24-6; VO, 20644-97-7; Zn, 7440-66-6; Al, 7429-90-5; Au, 7440-57-5; Ce, 7440-45-1; Cr, 7440-47-3; Fe, 7439-89-6; In, 7440-74-6; La, 7439-91-0; Nd, 7440-00-8; Pr, 7440-10-0; Sc, 7440-20-2; Sm, 7440-19-9; Y, 7440-65-5.

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Molecular Dipole Moment Charges from a New Electronegativity Scale

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Received June 28, 1984

A testing of Mande et al.'s new electronegativity scale is presented by comparing calculated dipole moment charges with those obtained from experimental data. An analysis is made of several equations in which the dipole moment charges are functions of the difference in electronegativity of the atoms forming the bond.

Introduction

The concept of electronegativity is a very convenient tool to understand chemical binding in molecules, alloys, and compounds.¹⁻¹² Several attempts have been performed in order to

obtain a quantitative measure of atomic electronegativities.^{1,13-18} Unfortunately, it has proven very difficult to achieve a unique

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unequivocal scale for "the power of an atom in a molecule to attract electrons towards itself", referred to by Pauling¹ as the conceptual definition of electronegativity, which is of utmost importance for estimating dipole moments,^{1,19} chemical shifts in PES,^{20,21} quadrupole coupling constants,^{19,22} and infrared intensities.²³

It has been shown earlier by Mande and Damle^{24,25} that screening constants for orbital energies may be obtained from Dirac's relativistic equation in conjunction with X-ray spectroscopic data. Mande et al.¹⁸ extended that work by calculating effective nuclear charges for the valence states of atoms of several elements. Using these values of effective charges, they constructed a new electronegativity scale, consistent with Pauling's original definition, in the same fashion as Allred and Rochow¹⁶ obtained one using Slater's screening constants. These authors discussed the merits of the new scale with respect to atomic properties only, and they were able to find very satisfactory correlations with other electronegativity scales and with experimental data. On the basis of such good results, we have considered it appropriate to continue the investigation of its qualities.

The purpose of this work is to extend the analysis of the new electronegativity scale by calculating dipole moment charges of diatomic molecules, since there are experimental data published^{26,27} for its estimation and other interesting comparisons have been made by means of already known electronegativity scales.^{28,29}

In the next sections we present the means by which we applied the electronegativity values to the calculation of molecular dipole moment charges. We display the results obtained for several computational schemes together with values calculated from other electronegativity scales and experimental data. Finally we present the analysis of numerical results in a comparative fashion, and the qualities of the new scale when applied to the determination of molecular properties are pointed out. It should be emphasized that, in keeping with traditional uses of electronegativity, the objective is to obtain conclusions that may help to recognize and establish basic trends in certain properties of molecules, not to establish rigorous results. From this point of view, the approximations taken throughout the article are permissible.

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Table I. Values of q_1 and Deviations Calculated with the Three Electronegativity Scales

molecule	Pauling		Allred-Rochow		Mande et al.		exptl q
	q_1	D_P	q_1	D_A	q_1	D_M	
LiF	0.895	0.056	0.914	0.075	0.919	0.080	0.839
NaF	0.910	0.031	0.908	0.029	0.952	0.073	0.879
KF	0.923	0.101	0.921	0.099	0.969	0.147	0.822
RbF	0.929	0.147	0.924	0.142	0.969	0.187	0.782
LiCl	0.632	-0.099	0.579	-0.152	0.555	-0.176	0.731
NaCl	0.668	-0.124	0.563	-0.229	0.671	-0.121	0.792
KCl	0.702	-0.099	0.602	-0.199	0.749	-0.052	0.801
RbCl	0.718	-0.066	0.610	-0.174	0.752	-0.032	0.784
LiBr	0.555	-0.038	0.543	-0.050	0.523	-0.070	0.593
NaBr	0.594	-0.164	0.527	-0.231	0.643	-0.115	0.758
KBr	0.632	-0.151	0.567	-0.216	0.724	-0.059	0.783
RbBr	0.650	-0.117	0.575	-0.192	0.727	-0.040	0.767
LiI	0.473	-0.172	0.319	-0.326	0.383	-0.262	0.645
NaI	0.514	-0.194	0.302	-0.406	0.514	-0.194	0.708
KI	0.555	-0.183	0.345	-0.393	0.610	-0.128	0.738
RbI	0.575	-0.177	0.353	-0.399	0.614	-0.138	0.752
BrF	0.302	0.149	0.370	0.217	0.409	0.256	0.153
BrCl	0.010	-0.045	0.002	-0.053	0.002	-0.053	0.055
ICl	0.039	-0.072	0.092	-0.019	0.041	-0.070	0.111
IBr	0.010	-0.052	0.068	0.006	0.027	-0.035	0.062
rms		0.126		0.224		0.137	

Table II. Values of q_2 and Deviations Calculated with the Three Electronegativity Scales

molecule	Pauling		Allred-Rochow		Mande et al.		exptl q
	q_2	D_P	q_2	D_A	q_2	D_M	
LiF	0.885	0.046	0.898	0.059	0.863	0.024	0.839
NaF	0.909	0.030	0.889	0.010	0.932	0.053	0.879
KF	0.931	0.109	0.912	0.090	0.966	0.144	0.822
RbF	0.940	0.158	0.916	0.134	0.967	0.185	0.782
LiCl	0.777	0.046	0.762	0.031	0.678	-0.053	0.731
NaCl	0.824	0.032	0.740	-0.052	0.838	0.046	0.792
KCl	0.866	0.065	0.794	-0.007	0.924	0.123	0.801
RbCl	0.885	0.101	0.804	-0.020	0.926	0.142	0.784
LiBr	0.740	0.147	0.745	0.152	0.659	0.066	0.593
NaBr	0.794	0.036	0.721	-0.037	0.828	0.070	0.758
KBr	0.843	0.060	0.779	-0.004	0.919	0.136	0.783
RbBr	0.865	0.098	0.790	0.023	0.922	0.155	0.767
LiI	0.694	0.049	0.598	-0.047	0.565	-0.080	0.645
NaI	0.757	0.049	0.565	-0.143	0.773	0.065	0.708
KI	0.814	0.076	0.647	-0.091	0.893	0.155	0.738
RbI	0.840	0.088	0.663	-0.089	0.897	0.145	0.752
BrF	0.170	0.017	0.211	0.058	0.214	0.061	0.153
BrCl	0.007	-0.048	0.002	-0.053	0.001	-0.054	0.055
ICl	0.030	-0.081	0.087	-0.024	0.032	-0.079	0.111
IBr	0.008	-0.054	0.066	0.004	0.022	-0.040	0.062
rms		0.081		0.074		0.108	

Molecular Dipole Moment Charges and Electronegativity

It has long been recognized that the dipole moment charge q of the atoms forming a diatomic molecule AB can be related to the difference between the two atomic electronegativities $X_B - X_A$. Pauling¹ proposed for the ionic character of the bond (i.e. static charge) the relationship

$$q_1 = 1 - \exp(-(X_B - X_A)^2/4) \quad (1)$$

This formula was chosen to agree with the then available experimental data of dipole moment charges $q = \mu/eR_e$, where μ is the dipole moment, R_e the internuclear distance and e the electronic charge. Several equations like (1) or other functions of $X_B - X_A$ have been applied to the calculation of various chemical-physics properties in a theoretical way.^{1,19-23}

However, Nethercot²⁸ found that these equations do not fit recent experimental data. He concluded that q could not be a simple function of $X_B - X_A$. A charge-transfer model based on Mulliken's^{13,14} definition of electronegativity suggested that the appropriate variable would be a normalized difference ($X_B -$

Table III. Values of q_3 and Deviations Calculated with the Three Electronegativity Scales

molecule	Pauling		Allred-Rochow		Mande et al.		exptl q
	q_3	D_p	q_3	D_A	q_3	D_M	
LiF	0.841	0.002	0.860	0.021	0.811	-0.028	0.839
NaF	0.876	-0.003	0.846	-0.033	0.911	0.032	0.879
KF	0.909	0.087	0.880	0.058	0.967	0.145	0.822
RbF	0.923	0.141	0.887	0.105	0.969	0.187	0.782
LiCl	0.711	-0.020	0.696	-0.035	0.613	-0.118	0.731
NaCl	0.764	-0.028	0.673	-0.119	0.781	-0.011	0.792
KCl	0.816	0.015	0.730	-0.071	0.898	0.097	0.801
RbCl	0.841	0.057	0.741	-0.043	0.902	0.118	0.784
LiBr	0.672	0.079	0.677	0.084	0.595	0.002	0.593
NaBr	0.730	-0.028	0.654	-0.104	0.768	0.010	0.758
KBr	0.787	0.004	0.713	-0.070	0.890	0.107	0.783
RbBr	0.814	0.047	0.725	-0.042	0.895	0.128	0.767
LiI	0.628	-0.017	0.541	-0.104	0.513	-0.132	0.645
NaI	0.690	-0.018	0.513	-0.195	0.707	-0.001	0.708
KI	0.752	0.014	0.584	-0.154	0.852	0.114	0.738
RbI	0.782	0.030	0.599	-0.153	0.858	0.106	0.752
BrF	0.193	0.040	0.228	0.075	0.230	0.077	0.153
BrCl	0.018	-0.037	0.006	-0.049	0.005	-0.050	0.055
ICl	0.053	-0.058	0.116	0.005	0.056	-0.055	0.111
IBr	0.020	-0.042	0.095	0.033	0.041	-0.021	0.062
rms		0.052		0.094		0.096	

Table IV. Values of q_4 and Deviations Calculated with the Three Electronegativity Scales

molecule	Pauling		Allred-Rochow		Mande et al.		exptl q
	q_4	D_p	q_4	D_A	q_4	D_M	
LiF	0.750	-0.089	0.763	-0.076	0.730	-0.109	0.839
NaF	0.775	-0.104	0.754	-0.125	0.802	-0.077	0.879
KF	0.800	-0.022	0.778	-0.044	0.857	0.035	0.822
RbF	0.813	0.031	0.783	0.001	0.859	0.077	0.782
LiCl	0.667	-0.064	0.657	-0.074	0.606	-0.125	0.731
NaCl	0.700	-0.092	0.643	-0.149	0.710	-0.082	0.792
KCl	0.733	-0.068	0.678	-0.123	0.791	-0.010	0.801
RbCl	0.750	-0.034	0.686	-0.098	0.795	0.011	0.784
LiBr	0.643	0.050	0.646	0.053	0.595	0.002	0.593
NaBr	0.679	-0.079	0.631	-0.127	0.702	-0.056	0.758
KBr	0.714	-0.069	0.668	-0.115	0.785	0.022	0.783
RbBr	0.732	-0.035	0.675	-0.092	0.789	0.022	0.767
LiI	0.615	-0.030	0.561	-0.084	0.543	-0.102	0.645
NaI	0.654	-0.054	0.543	-0.165	0.664	-0.044	0.708
KI	0.692	-0.046	0.588	-0.150	0.758	0.020	0.738
RbI	0.712	-0.040	0.597	-0.155	0.762	0.010	0.752
BrF	0.300	0.147	0.332	0.179	0.334	0.181	0.153
BrCl	0.067	0.012	0.032	-0.023	0.027	-0.028	0.055
ICl	0.133	0.022	0.219	0.108	0.138	0.027	0.111
IBr	0.071	0.009	0.193	0.131	0.114	0.052	0.062
rms		0.066		0.116		0.073	

$X_A)/\bar{X}$, where \bar{X} is the arithmetic mean (AM) or the geometric mean (GM) of the two atomic electronegativities.²⁸⁻³¹ Nethercot proposed the following formulas to match experimental data with electronegativity values on an empirical basis:²⁸

$$q_2 = 1 - \exp(-3(X_B - X_A)^2/X_{AM}^2) \quad (2)$$

$$q_3 = 1 - \exp(-(X_B - X_A)^{3/2}/X_{GM}^{3/2}) \quad (3)$$

In spite of this, Barbe³² has recently proposed an extremely simple expression for the dipole charge based on empirical arguments:

$$q_4 = (X_B - X_A)/X_B \quad (4)$$

with $X_B > X_A$.

In the next section we compare eq 1-4, showing the incapability of eq 1 to give reliable estimations of q . We also confront the new electronegativity scale with other scales and with values

Table V. Comparison between ab Initio Charges and Values Calculated with Eq 1-4 by Using Pauling's Electronegativity Scale for the First- and Second-Row Hydrides

molecule	q_{ab}	q_1	D_1	q_2	D_2	q_3	D_3	q_4	D_4
LiH	0.781	0.30	-0.48	0.57	-0.21	0.52	-0.26	0.55	-0.21
BeH	0.043	0.12	0.08	0.19	0.15	0.21	0.17	0.32	0.29
BH	0.304	0.01	-0.29	0.01	-0.29	0.03	-0.27	0.09	-0.15
CH	0.302	0.02	-0.28	0.02	-0.28	0.04	-0.26	0.12	-0.15
NH	0.337	0.15	-0.19	0.13	-0.21	0.16	-0.18	0.27	-0.05
OH	0.387	0.34	-0.05	0.27	-0.12	0.27	-0.12	0.37	0.01
HF	0.441	0.56	0.12	0.40	-0.04	0.38	-0.06	0.45	0.03
NaH	0.769	0.34	-0.43	0.65	-0.12	0.59	-0.18	0.59	-0.12
MgH	0.179	0.22	0.04	0.40	0.22	0.38	0.20	0.46	0.31
AlH	0.014	0.12	0.11	0.19	0.18	0.21	0.20	0.32	0.31
SiH	0.038	0.04	0.00	0.06	0.02	0.09	0.05	0.18	0.16
PH	0.080	0.00	-0.08	0.00	-0.08	0.01	-0.07	0.05	-0.02
SH	0.137	0.02	-0.12	0.02	-0.12	0.04	-0.10	0.12	0.01
ClH	0.196	0.15	-0.05	0.13	-0.07	0.16	-0.04	0.27	0.09
rms			0.23		0.18		0.18		0.18

Table VI. Values of Δ_1 , Δ_2 , and Δ_3 for the Three Electronegativity Scales

molecule	Pauling			Allred-Rochow			Mande et al.		
	Δ_1	Δ_2	Δ_3	Δ_1	Δ_2	Δ_3	Δ_1	Δ_2	Δ_3
LiF	3.0	1.20	1.50	3.13	1.24	1.57	3.17	1.15	1.41
NaF	3.1	1.27	1.63	3.09	1.21	1.52	3.48	1.34	1.80
KF	3.2	1.33	1.79	3.19	1.27	1.65	3.72	1.50	2.27
RbF	3.25	1.33	1.79	3.21	1.29	1.68	3.73	1.51	2.29
LiCl	2.0	1.00	1.15	1.86	0.98	1.12	1.80	0.87	0.97
NaCl	2.1	1.08	1.28	1.82	0.95	1.08	2.11	1.10	1.32
KCl	2.2	1.16	1.42	1.92	1.03	1.20	2.35	1.31	1.73
RbCl	2.25	1.16	1.42	1.94	1.04	1.22	2.36	1.32	1.75
LiBr	1.8	0.95	1.08	1.77	0.95	1.09	1.72	0.85	0.94
NaBr	1.9	1.03	1.20	1.73	0.92	1.04	2.03	1.08	1.29
KBr	2.0	1.11	1.34	1.83	1.00	1.16	2.27	1.29	1.70
RbBr	2.05	1.11	1.34	1.85	1.03	1.19	2.28	1.30	1.72
LiI	1.6	0.89	0.99	1.24	0.78	0.85	1.39	0.75	0.80
NaI	1.7	0.97	1.11	1.20	0.75	0.80	1.70	0.99	1.15
KI	1.8	1.06	1.25	1.30	0.83	0.92	1.94	1.22	1.54
RbI	1.85	1.06	1.25	1.32	0.85	0.94	1.95	1.23	1.56
BrF	1.2	0.35	0.36	1.36	0.40	0.41	1.45	0.40	0.41
BrCl	0.2	0.07	0.07	0.09	0.03	0.03	0.08	0.03	0.03
ICl	0.4	0.14	0.14	0.62	0.25	0.25	0.41	0.15	0.15
IBr	0.2	0.07	0.07	0.53	0.21	0.22	0.33	0.12	0.12

Table VII. Values of Δ_1 , Δ_2 , and Δ_3 for the First- and Second-Row Hydrides with Pauling's Electronegativity Scale

molecule	Δ_1	Δ_2	Δ_3	molecule	Δ_1	Δ_2	Δ_3
LiH	1.2	0.75	0.81	NaH	1.3	0.92	0.34
BeH	0.7	0.38	0.39	MgH	1.0	0.62	0.22
BH	0.2	0.10	0.10	AlH	0.7	0.39	0.12
CH	0.3	0.13	0.13	SiH	0.4	0.20	0.04
NH	0.8	0.31	0.31	PH	0.1	0.05	0.00
OH	1.3	0.46	0.47	SH	0.3	0.13	0.02
HF	1.8	0.58	0.61	HCl	0.8	0.31	0.15

estimated from experimental data.

Results

We have chosen Pauling's¹ and Allred and Rochow's¹⁶ electronegativity scales in order to compare calculated charges with those computed from the new electronegativity scale¹⁸ and experimental data (i.e. spectroscopic values of μ and R_e).^{26,27}

The molecules selected were those reported in ref 26 and 27, where accurate experimental values of μ and R_e were given.

In Tables I-IV we show the results obtained by applying eq 1-4 to the three electronegativity scales. The columns headed by D_p , D_A , and D_M are the deviations $q(\text{calcd}) - q(\text{exptl})$ for each electronegativity scale, where $q(\text{calcd})$ is the dipole moment charge calculated with the corresponding equation and $q(\text{exptl})$ is the dipole charge computed from the experimental values of μ and R_e . We also report the root mean squared deviations (rms).

In Table V we present the values of q calculated from μ and R_e obtained from ab initio calculations for the first- and second-row hydrides,³¹ together with results of applying eq 1-4 and Pauling's

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scale. We include the individual deviations and rms for each formula.

Finally in Tables VI and VII we display the values of $\Delta_1 = X_B - X_A$, $\Delta_2 = (X_B - X_A)/((X_B - X_A)/2)$, and $\Delta_3 = (X_B - X_A)/(X_B X_A)^{1/2}$, for the different molecules and electronegativity scales.

Discussion

Though the set of molecules studied is a little reduced, we believe that the range of dipole moment charges included is sufficiently broad to state some general conclusions.

Comparing the rms values obtained with eq 1-4 for the three scales, we concluded that eq 1 is incapable of producing reliable results of the dipole moment charge, in contrast with eq 2-4, which are of similar qualities. There is no advantage in using the more complex eq 2 and 3 instead of the much simpler eq 4. It may be seen that for the last equation there are many negative deviations; this suggests that if we include an empirical correction factor f in the expression for q

$$q_4 = f(X_B - X_A)/X_B \quad (5)$$

with $X_B > X_A$, we would obtain a better correlation between these values and those calculated from experimental values of μ and R_e . Indeed, that is so and the rms reduces to 0.054, 0.090, and 0.071 for each of the three scales (Pauling, Allred-Rochow, and Mande et al., respectively). The correction factors are 1.058,

1.119, and 1.021 for the three scales.

If we compare the electronegativity scales, we see that Mande et al.'s scale is nearly as good as Pauling's and perhaps a little better than Allred-Rochow's scale. This last observation is in agreement with the fact that Allred-Rochow's scale and Mande et al.'s scale have the same physical basis, but the latter calculates the effective charges in a more accurate fashion.

For the hydrides in Table V, we see that the results are worse than those obtained for the alkali-metal halides and the interhalogenides. The reason is in part due to the fact that electronegativity scales report values only for the most common oxidation states, and the great majority of molecules in the table do not fulfill this condition. As pointed out by Nethercot²⁹ and Barbe,³² each value of electronegativity must be corrected for this effect. To obtain an electronegativity scale for various oxidation states is a task that deserves more effort. Research along this line is being made in our laboratory, and results will be published in a forthcoming paper.

Acknowledgment. This work has been made possible thanks to the financial support of CONICET, República Argentina. INIFTA is sponsored by the Consejo Nacional de Investigaciones Científicas y Técnicas, the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires, and the Universidad Nacional de La Plata.

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Kinetics of Electron Transfer from Tris(picolinato)chromate(II) to Iron(III)

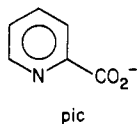
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Received September 24, 1984

The mechanism of the electron-transfer reaction from tris(picolinato)chromate(II) to iron(III) has been studied by spectrophotometry and stopped-flow techniques. The rate constants and the activation parameters for the inner-sphere process involving the formation and decay of the binuclear intermediate have been determined. The relevant thermodynamic and kinetic parameters for the formation of tris(picolinato)chromate(II), required for understanding the redox mechanism, have been determined from spectrophotometric and stopped-flow experiments. Some of the results were verified by T -jump measurements. All the values have been reported at 25 °C and ionic strength 2.3 M unless otherwise indicated. For the binuclear intermediate, the following rate constants were obtained: $k(\text{formation}) = 14.1 \text{ M}^{-1} \text{ s}^{-1}$; $k(\text{decay}) = 5.6 \times 10^{-4} \text{ s}^{-1}$.

Introduction

The corrosion products in nuclear reactors are mainly mixed-transition-metal oxides,¹ the major constituents being the oxides of Cr(III) and Fe(III). In order to facilitate their rapid removal, a practical method for their dissolution has to be devised.²⁻⁴ Recently, a method involving the use of $V(\text{pic})_3^-$, a powerful



reductant, was developed for dissolving metal oxides.⁵ It has been found that this process is inefficient in dissolving oxides that have

a high chromium content.¹ Consequently, tris(picolinato)chromate(II), which is a very stable complex,⁶⁻⁸ was tried as a possible decontaminating agent.

The mechanism of the homogeneous electron-transfer reaction between the complex, tris(picolinato)chromate(II), and Fe^{3+} was studied prior to investigating the heterogeneous reaction. This reaction, which is relatively slow, proceeds by an inner-sphere mechanism. Unlike the case of outer-sphere electron-transfer reactions, for which detailed theoretical studies are available and reasonably well supported by experimental evidence, quantitative theoretical predictions for inner-sphere reactions appear to be more elusive.⁹ The main focus of the investigations on this subject has been in detailing the actual mechanism of the electron-transfer process in complementary redox reactions between transition-metal ion complexes. The mechanism of these reactions depends upon the substitution properties of the reductant (usually the more labile reactant), the availability (or the unavailability) of a bridging

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