

Experimental details will be reported elsewhere. This work was supported by the Hungarian Academy of Science.

G. FODOR  
K. NÁDOR

Institute of Organic Chemistry,  
University, Szeged. Sept. 28.

- <sup>1</sup> Fodor, G., et al., (a) *J. Org. Chem.*, **14**, 337 (1949); (b) *ibid.*, **15**, 226 (1950).  
<sup>2</sup> Fodor, G., Kiss, J., and Sallay, I., *J. Chem. Soc.*, 1858 (1951).  
<sup>3</sup> Fodor, G., and Kiss, J., (a) *Nature*, **164**, 917 (1949); (b) *Research*, **4**, 382 (1951); (c) *Research*, **4**, 381 (1951).  
<sup>4</sup> McCasland, *J. Amer. Chem. Soc.*, **73**, 2295 (1951).  
<sup>5</sup> (a) Willstätter, R., and Bode, A., *Ber.*, **33**, 416 (1900). (b) Gadamer, J., *Arch. Pharm.*, **239**, 298 (1901). (c) Barrowcliff, M., and Tutin, F., *J. Chem. Soc.*, **95**, 1967 (1909). (d) Willstätter, R., and Bommer, M., *Lieb. Ann.*, **422**, 18 (1921).  
<sup>6</sup> (a) Kimura, K. K., and Unna, K. R., *J. Pharmacol. Exp. Therap.*, **98**, 286 (1950). (b) Issekutz, sen., B., and Nádor, K., meeting of the Hungarian Society for Physiology at Szeged, June 1950.  
<sup>7</sup> Prepared by Polonovsky, M., and Polonovski, M., *Bull. Soc. Chim.*, **39**, 1147 (1926), who suggested it had the structure of an acylamide salt; our electrometric titrations proved the correctness of this assumption.

### Anion Affinity and Polarizing Power of Cations

It is suggested that the ionization potential, *I* (first for univalent cations, second for divalent cations, third for trivalent cations, and so on), be used as a relative measure of the power of a cation to attract an anion (its 'anion affinity'), and of its polarizing power. Its use thus may be demonstrated by some of the comparisons below. The general concept used here of the ability of cations to polarize and deform anions follows that discussed in the writings of Fajans<sup>1,2</sup> and of others, and the homopolar bonds referred to below are regarded as strongly polarized ionic bonds.

#### (1) Univalent ions

(*I* increases →) :

	Cs <sup>+</sup>	Rb <sup>+</sup>	K <sup>+</sup>	Na <sup>+</sup>	Li <sup>+</sup>	Tl <sup>+</sup>	Ag <sup>+</sup>	Cu <sup>+</sup>	Au <sup>+</sup>
<i>I</i> (volts)	3.9	4.2	4.34	5.14	5.4	6.1	7.57	7.7	9.22
Radius (A.)	1.67	1.47	1.33	0.97	0.68	1.47	1.27	0.96	1.37

Radii are included, based mainly on those of Pauling<sup>3</sup>, as revised, with additions, by Ahrens<sup>4</sup>.

A progressive change in bond type (ionic → covalent) with a given partner (O<sup>2-</sup>, S<sup>2-</sup>, Cl<sup>-</sup>, etc.) is usually apparent when going from left to right, with thallium frequently occupying an intermediate position. For some purposes of comparison, Li<sup>+</sup> should be omitted because of its small size.

#### (2) Medium-sized (0.6–0.8 A.) divalent cations

: (*I* increases →) :

	Mg <sup>2+</sup>	Mn <sup>2+</sup>	Fe <sup>2+</sup>	Co <sup>2+</sup>	Zn <sup>2+</sup>	Ni <sup>2+</sup>	Pt <sup>2+</sup>	Pd <sup>2+</sup>	Cu <sup>2+</sup>
<i>I</i> (volts)	15.03	15.64	16.24	17.4	17.95	18.2	19.3	19.9	20.3
Radius (A.)	0.66	0.80	0.74	0.73	0.74	0.69	0.80	0.80	0.72

With increase in anion affinity there is again a progressive change in chemical, crystal chemical and stereochemical properties, and in the ability to form stable complexes. Manganese and nickel frequently occupy positions intermediate between the two extremes, magnesium and platinum, palladium and copper.

The possibility that the coplanar stereochemistry of divalent copper, palladium, platinum (all partners

except fluorine) and sometimes nickel could arise as a result of extreme deformation (polarization) of the partner suggests itself as a possible alternative to the concept of hybridization of bond orbitals as postulated by Pauling<sup>5</sup>.

When arranged in order of increasing anion affinity, large (0.97–1.20 A.) divalent cations, Ba<sup>2+</sup>, Ca<sup>2+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup> and Hg<sup>2+</sup>, also show progressive changes of properties as above. These ions have the 8:4 (fluorite) structure with the rigid anion F<sup>-</sup>, whereas the 6:3 (rutile) structure is common for divalent ions of the medium-sized group.

The greatest ionization potential of any divalent metal is that of Ag<sup>2+</sup> (22.0 volts; radius 0.89 A.) and is a probable cause for the unusual properties of this ion and for the instability of all its compounds, AgF<sub>2</sub> included.

L. H. AHRENS

Department of Geology,  
Massachusetts Institute of Technology,  
Cambridge, Mass.  
Sept. 25.

- <sup>1</sup> Fajans, K., *Z. Elektrochem.*, **34**, 502 (1928).  
<sup>2</sup> Fajans, K., and Joos, G., *Z. Phys.*, **23**, 1 (1924).  
<sup>3</sup> Pauling, L., "The Nature of the Chemical Bond", 346 (2nd edit., 1945).  
<sup>4</sup> Ahrens, L. H. (in the press).  
<sup>5</sup> Pauling, L., "The Nature of the Chemical Bond", 98 (2nd edit., 1945).

### Reaction Velocities and Activation Energies of some 'Instantaneous' Complex Ion Reactions

IN connexion with an investigation of the slow time reactions in the chromic thiocyanate system in aqueous solution, one of us (J. B.) had the idea that it might be possible to estimate the energies of activation in 'instantaneous' complex ion reactions by investigating the reactions in alcoholic solutions at low temperatures. These expectations have been to a great extent fulfilled.

The introductory experiments were carried out in test-tubes at approximately -75° C. in a bath of solid carbon dioxide and 96 per cent ethanol in an unsilvered litre Dewar flask, and at about -100° C. in a bath of melting methanol (made by means of liquid air and kept in circulation by aeration). Various complex systems with strongly coloured complexes were examined visually in methanol solution, and the following new measurable reactions with times of half-completion varying from many hours to a few seconds in 0.05–0.001 molar solutions were discovered:

(1) Ferric ions reacted measurably with thiosulphate to form a stable violet complex, as also with phenols at -75° C. The colour reaction with sulphosalicylic acid occurred several times faster than with salicylic acid, probably due to the electro-negative influence of the sulphonic group.

(2) Nickel ions (Ni<sup>2+</sup>) gave slow reactions with dimethylglyoxime, pyridine and ethylenediamine at -75°, while Cu<sup>2+</sup> reacted in a few seconds with ethylenediamine at -100° C., but instantaneously with ammonia and pyridine.

(3) Thiocyanate ions gave delayed reactions with PdCl<sub>4</sub><sup>-</sup>, AuCl<sub>4</sub><sup>-</sup>, PtCl<sub>6</sub><sup>-</sup>, Fe<sup>3+</sup> at -75° C. with rates increasing in the order mentioned, and at -100° C. also with Co<sup>2+</sup>. Cupric ions still reacted instantaneously at this temperature.