Reaction Mechanism in Ionic Systems

Bal Krishna

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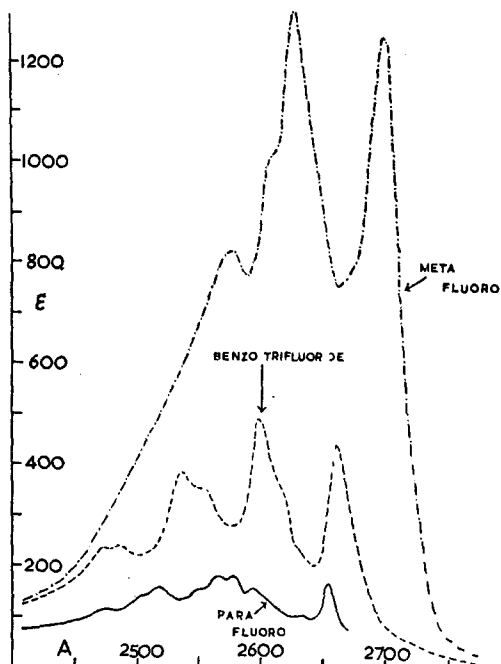J. Chem. Phys. **39**, 3341 (1963); 10.1063/1.1734199

FIG. 2.

agreed closely with those given in A.P.I. reference curves (Serial Nos. 11 and 12).

Two points of interest may be noted. First, along the series *ortho*-fluorotoluene, *meta*-fluorotoluene, *para*-fluorotoluene, the onset of absorption as indicated by the intense band of longest wave-length, moves towards longer wave-lengths. With the substituted benzotrifluorides, however, the *para*-derivative is anomalous in having its first band at shorter wave-lengths than *meta*-fluorobenzotrifluoride or benzotrifluoride itself.

This anomaly is further brought out by the extinction coefficient for the bands involved. The values (liters/gmoles/cm/ $\log_{10}$ units) are given in Table I, in which the remarkable fall in

TABLE I. Values of ϵ for long wave-length band.

Toluene	240	Benzotrifluoride	440
o-fluorotoluene	860		
m-fluorotoluene	690	m-fluorobenzotrifluoride	1250
p-fluorotoluene	1160	p-fluorobenzotrifluoride	168

the case of *para*-fluorobenzotrifluoride is to be contrasted with the high value in *para*-fluorotoluene. The results indicate that the electronic influences introduced by the presence of $-CF_3$ and $-F$ groups, both separately and together, may be considerable, and suggests a topic for theoretical consideration.

[1] W. T. Cave and H. W. Thompson, in press.

Reaction Mechanism in Ionic Systems

BAL KRISHNA
Department of Chemistry, Allahabad University, Allahabad, India
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THE velocity and mechanism of chemical reaction between charged ions, are, to a great extent dependent upon the nature of the charges of the reacting species. Where the reaction occurs between oppositely charged ions, the process is likely to be helped by the Coulombic attraction present between the reacting ions, while in case of similarly charged ions, the process has to be slow, adopt a different mechanism, and take the aid of a catalyst in order to overcome the resistance of the reaction present in the form of Coulombic repulsion. Incidentally, it may be pointed out that a detailed study of the reactions between similarly charged ions is likely to be of great value in understanding the exact role of a catalyst, and an exact physical significance of such terms as "collision complexes," "energy of activation" and "potential barriers" in any particular instance.

Moreover as pointed out by Bronsted[1] a change in the electrical properties of the medium in such cases greatly affects the reaction velocity. An increase of ionic strength in case of a reaction between similarly charged ions leads to an enhancement in the value of the specific reaction rate, while in case of oppositely charged ions, the value of specific reaction rate decreases with an increase in the ionic strength of the medium. These two effects are expressed by the following equation for a bimolecular reaction:

$$\log K = \log Ko + Z_A Z_B(\mu)^{\frac{1}{2}} \tag{1}$$

where Z represents the charge of the ions, μ the ionic strength, K the specific reaction rate, and Ko is defined by the following equation:
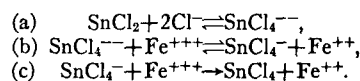
$$K = Ko(f_A f_B / f_x) \tag{2}$$

where f_A and f_B are activity coefficients the ions A and B respectively, and f_x the activity coefficient of the "collision complex." Bronsted has deduced these equations semi-thermodynamically and they are of great help in elucidating the mechanism of ionic reactions.

The study of the reaction between ferric ion and the stannous ion affords an interesting example from this point of view. The over-all ionic reaction can be represented as follows:

$$2Fe^{+++} + Sn^{++} \rightarrow 2Fe^{++} + Sn^{++++}.$$
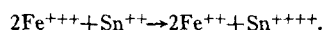
The reaction was first studied by Noyes[3] who found that the reaction is termolecular in absence of hydrochloric acid, and bimolecular in presence of it. Weiss[4] points out that the experimental results obtained by Noyes, can be well explained if one assumes that the reaction proceeds in the following way:

(a) $SnCl_2 + 2Cl^- \rightleftharpoons SnCl_4^{--}$,
(b) $SnCl_4^{--} + Fe^{+++} \rightleftharpoons SnCl_4^- + Fe^{++}$,
(c) $SnCl_4^- + Fe^{+++} \rightarrow SnCl_4 + Fe^{++}$.

It is obvious that the electron transfer occurs between oppositely charged ions. But apart from theoretical considerations,[2] there has come no evidence that the rate determining process occurs between two oppositely charged ions.

In order to understand that exact mechanism of the reaction between ferric ion and stannous ion, the present author has studied the kinetics of this reaction in detail at the temperature of melting ice. It has been found that the increase in ionic strength of the medium produces a retardation in reaction velocity in all cases except where the ionic strength is increased by adding nitric acid, or hydrochloric acid, or other chlorides. Chloride ion as was already known produces a powerful accelerating effect.

Assuming the validity of Bronsted's equation, we are forced to conclude that the rate determining process occurs between oppositely charged ions. My experiment therefore provides one of the ways in which the intermediate links of the reaction in ionic media can be traced, and a new utility of Bronsted's equation.

[1] Bronsted, Chem. Rev. **5**, 231 (1928).
[2] Hinshelwood, J. Chem. Soc., p. 694 (1947).
[3] Noyes, Zeits. f. physik. Chemie **16**, 576 (1895).
[4] Weiss, J. Chem. Soc., p. 309 (1944)