

7. Kinetic Study of the Reaction of Hexacyanoferrate(III) with Iodide Ion in Acid Medium.

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The rate of the reaction between potassium ferricyanide and iodide has been measured by a microtitration method. The reaction is specifically catalysed by the hydrogen ion and no evidence of general acid catalysis has been found. The orders for the uncatalysed path are confirmed as two with respect to iodide and one with respect to ferricyanide ion; the orders of the catalysed path are determined as one each with respect to ferricyanide, hydrogen, and iodide ion. This decrease in the order with respect to iodide is attributed to distortion of the co-ordination sphere of $\text{Fe}(\text{CN})_6^{3-}$ produced by the hydrogen ion; the fact that a decrease in the order is also observed in the presence of La^{3+} is considered a confirmation of this view.

THE reaction between ferricyanide ion and iodide ion has been studied by several authors. The reaction is of the first order with respect to $\text{Fe}(\text{CN})_6^{3-}$, second order with respect to I^- , is inhibited by $\text{Fe}(\text{CN})_6^{4-}$ ions,¹ and is accelerated by hydrogen chloride;² its rate is specifically influenced by the different alkali-metal ions;³ at low iodide concentration the order with respect to iodide ion decreases towards one,⁴ as happens also in the reaction between iodide and iodate.⁵ These investigations have been performed at rather high concentrations [0.1 — 1.0M in $\text{Fe}(\text{CN})_6^{3-}$], and sometimes the ionic strength has not been kept constant. More recently, one of us measured the initial reaction rate by a microtitration method⁶ so as to eliminate complications due to the products. The results of Wagner¹ and of Friedmann and Anderson³ have been confirmed for much lower concentrations. Moreover, it was observed that the reaction shows a prominent Olson-Simonson effect,⁷ that the rate increases when the valency of the added cation increases, and that it decreases in the presence of tetra-alkylammonium salts.⁸ It was concluded that the salt effects in this reaction involve a considerable amount of non-electrostatic action.

¹ Wagner, *Z. phys. Chem.*, 1924, **113**, 261.

² Von Kiss, *Rec. Trav. chim.*, 1933, **52**, 289.

³ Friedmann and Anderson, *J. Amer. Chem. Soc.*, 1939, **61**, 116.

⁴ Bøchmann and Sandved, *Tidsskr. Kjem. Bergvesen Met.*, 1940, **20**, 106.

⁵ Abel and Hilferdings, *Z. phys. Chem.*, 1928, **136**, 186.

⁶ Indelli, *Ann. Univ. Ferrara, Nuova Serie*, 1960, **1**, 129.

⁷ Olson and Simonson, *J. Chem. Phys.*, 1949, **17**, 1167.

⁸ Indelli, *J. Phys. Chem.*, 1961, **65**, 972.

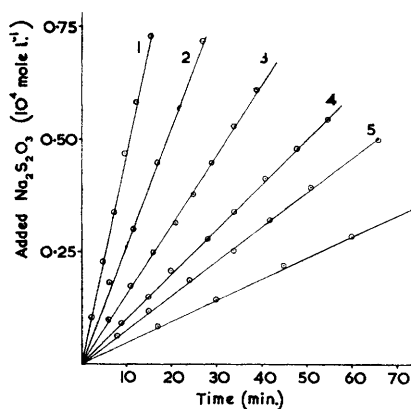
The microtitration method can be used to study the acid catalysis of this reaction. In particular, we thought it interesting to determine whether the acid catalysis is specific or general and whether the reaction orders are the same in the presence of acid as in its absence.

EXPERIMENTAL

The salts and the water were the same as those used in another paper.⁶ The solutions of acetic, formic, and perchloric acid were standardized against 0.1M-sodium hydroxide and were frequently tested. The experimental method was essentially as before⁶ and consisted of repeated titration of the iodine in the reaction mixture by means of sodium thiosulphate added through an "Aglar" microsyringe. Some starch was added to act as an indicator. A slight modification was introduced, consisting in using a double-walled glass vessel as reactor, and in circulating water from a thermostat-bath through the mantle. This permitted better determination of the end-point and better control of the air-oxidation of the iodide; the rate of the latter reaction, however, was negligible. The reaction proceeded to the extent of only 0.2—0.4%; in all cases the reaction rate was independent of the time, as is shown in Fig. 1. The

FIG. 1. Typical kinetic runs for the reaction of ferricyanide with iodide ions. In all runs, $[K_3Fe(CN)_6] = 0.01$ mole l^{-1} .

Run 1: $[KI] = 0.07$, $[La(NO_3)_3] = 0.01$. Run 2: $[KI] = 0.05$, $[La(NO_3)_3] = 0.01$. Run 3: $[KI] = 0.04$, $[HClO_4] = 0.0075$, $I = 0.15$. Run 4: $[KI] = 0.04$, $[HClO_4] = 0.002$, $I = 0.5$. Run 5: $[KI] = 0.04$, $[H\cdot CO_2H] = 0.1$, $[H\cdot CO_2Na] = 0.05$, $I = 0.5$. Run 6: $[KI] = 0.02$, $[HClO_4] = 0.005$, $I = 0.15$.



ionic strength I was kept constant by addition of sodium nitrate, whereas potassium salts were used as reactants because of their greater ease of purification. We did not use potassium salts to keep the ionic strength constant because of the highly specific effects that K^+ shows in other electron-transfer reactions.⁹⁻¹¹

The pH's of the buffer solutions were calculated by means of the equation¹²

$$pH = pK + \log_{10} (C_{\text{salt}}/C_{\text{acid}})$$

with 4.76 and 3.75 for the acetic and formic acid, respectively.¹³ No correction was made for the change in the pK with ionic strength, because the purpose of the buffer solutions was only to ascertain, qualitatively, whether the acid catalysis was general or specific. Anyway, since these runs were performed at constant ionic strength, the activity coefficients were also constant and under such conditions the calculated was proportional to the real hydrogen-ion concentration.

RESULTS

Acid Catalysis.—Table 1 reports the values of the reaction rate in the presence of different concentrations of perchloric acid at $I = 0.15$ and 0.50. Acid catalysis is apparent. The reaction rate, therefore, is given by the sum of two terms: one independent of, and the other

⁹ Howells, *J.*, 1946, 203; Indelli and Prue, *ibid.*, 1959, 107; Carassiti and Dejak, *Atti Accad. Sci. Ist. Bologna*, 1955, **11**, 1.

¹⁰ Sheppard and Wahl, *J. Amer. Chem. Soc.*, 1957, **79**, 1020.

¹¹ Wahl, *Z. Elektrochem.*, 1960, **64**, 90.

¹² Glasstone, "Textbook of Physical Chemistry," Macmillan and Co., London, 1948, p. 1007.

¹³ Ref. 12, p. 981.

dependent on, the hydrogen-ion concentration. The constancy of the values reported in the columns $v_{\text{H}}/[\text{H}^+]$ in Table 1 shows that there is a linear relation between reaction rate and acid concentration.

TABLE 1.

Overall reaction rates, $10^9v = -10^9d[\text{Fe}(\text{CN})_6^{3-}]/dt$ (mole l.⁻¹ sec.⁻¹), catalysed-reaction rates, $10^9v_{\text{H}} = 10^9(v - v_{\text{W}})$ (mole l.⁻¹ sec.⁻¹), and rate constants of pseudo-first order, $10^6v_{\text{H}}/[\text{H}^+]$ (sec.⁻¹), for the reaction of $\text{Fe}(\text{CN})_6^{3-}$ with I^- at 25°.

$$[\text{KI}] = 4 \times 10^{-2}, [\text{K}_3\text{Fe}(\text{CN})_6] = 1 \times 10^{-2} \text{ mole l.}^{-1}.$$

$10^3[\text{HClO}_4]$ (mole l. ⁻¹)	I	10^9v (mole l. ⁻¹ sec. ⁻¹)	10^9v_{H} (mole l. ⁻¹ sec. ⁻¹)	$10^6v_{\text{H}}/[\text{H}^+]$ (sec. ⁻¹)	$10^3[\text{HClO}_4]$ (mole l. ⁻¹)	I	10^9v (mole l. ⁻¹ sec. ⁻¹)	10^9v_{H} (mole l. ⁻¹ sec. ⁻¹)	$10^6v_{\text{H}}/[\text{H}^+]$ (sec. ⁻¹)
—	0.15	4.2 (v_{W})	—	—	7.5	0.15	25.7	21.5	2.9
2.0	0.15	9.8	5.6	2.8	—	0.50	10.6 (v_{W})	—	—
3.0	0.15	12.2	8.6	2.7	1.0	0.50	13.6	3.0	3.0
3.5	0.15	13.9	9.7	2.7	2.0	0.50	16.7	6.1	3.1
4.0	0.15	15.2	11.0	2.7	3.0	0.50	20.1	9.5	3.2
5.0	0.15	18.0	13.8	2.8	4.0	0.50	23.0	12.4	3.1
6.0	0.15	20.6	16.4	2.7	5.0	0.50	26.6	16.0	3.2

TABLE 2.

Reaction rates, 10^9v (mole l.⁻¹ sec.⁻¹), in acetic acid–sodium acetate and in formic acid–sodium formate buffer solutions at 25°.

$$[\text{KI}] = 4 \times 10^{-2}, [\text{K}_3\text{Fe}(\text{CN})_6] = 1 \times 10^{-2} \text{ mole l.}^{-1}.$$

$[\text{HA}]$ (mole l. ⁻¹)	$[\text{NaA}]$ (mole l. ⁻¹)	I	pH	10^9v (mole l. ⁻¹ sec. ⁻¹)	$[\text{HA}]$ (mole l. ⁻¹)	$[\text{NaA}]$ (mole l. ⁻¹)	I	pH	10^9v (mole l. ⁻¹ sec. ⁻¹)
<i>Acetic acid</i>					<i>Formic acid</i>				
0.10	0.010	0.15	3.8	5.3	0.01	0.005	0.50	3.4	12.5
0.25	0.025	0.15	3.8	5.4	0.05	0.025	0.50	3.4	12.7
0.50	0.050	0.15	3.8	5.4	0.10	0.050	0.50	3.4	12.5
0.10	0.002	0.15	3.1	6.0					
0.10	0.005	0.15	3.4	5.7					
0.10	0.010	0.15	3.8	5.3					
0.10	0.020	0.15	4.1	5.0					

Differentiation between General and Specific Acid Catalysis.—Table 2 gives the rates at different buffer concentrations for the system acetic acid–sodium acetate at an ionic strength $I = 0.15$, and for the system formic acid–sodium formate at an ionic strength $I = 0.50$, the ratio acid : salt being kept constant. The rates for different ratios acetic acid : sodium acetate are also reported. No evidence can be obtained for general acid catalysis, whereas an increase in the sodium acetate concentration, the concentration in acetic acid being kept constant, produces a decrease in the rate parallel to the increase in pH. A linear relation is observed between the rate and the hydrogen-ion concentration in this case, too.

Reaction Orders.—For neutral solutions we have confirmed the orders 2 with respect to iodide and 1 with respect to ferricyanide ion (details are not reported for the sake of brevity). Table 3

TABLE 3.

Reaction rates, 10^9v (mole l.⁻¹ sec.⁻¹) at different concentrations of KI, $\text{K}_3\text{Fe}(\text{CN})_6$, and HClO_4 (mole l.⁻¹), at 25°.

$[\text{HClO}_4] = 0.005$ $I = 0.15$	{	$[\text{KI}] \dots\dots\dots$	0.01	0.02	0.04	0.08	0.04	0.04
		$[\text{K}_3\text{Fe}(\text{CN})_6] \dots\dots$	0.01	0.01	0.01	0.01	0.005	0.015
		$10^9v \dots\dots\dots$	3.5	7.6	18.0	47.1	8.6	26.7
$[\text{HClO}_4] = 0.003$ $I = 0.50$	{	$[\text{KI}] \dots\dots\dots$		0.01	0.02	0.04	0.08	
		$[\text{K}_3\text{Fe}(\text{CN})_6] \dots\dots$		0.01	0.01	0.01	0.01	
		$10^9v \dots\dots\dots$		2.8	7.2	20.1	59.3	

reports the results obtained for different concentrations in potassium iodide and ferricyanide in an acid medium. The rates for the catalysed path are obtained by correcting for the uncatalysed reaction on the basis of the known reaction orders and of the rates for the neutral solutions

reported in Table 1. In Fig. 2 the logarithms of these corrected rates are plotted against the logarithms of the concentrations. The order with respect to ferricyanide is still 1, and the order with respect to iodide also becomes 1.

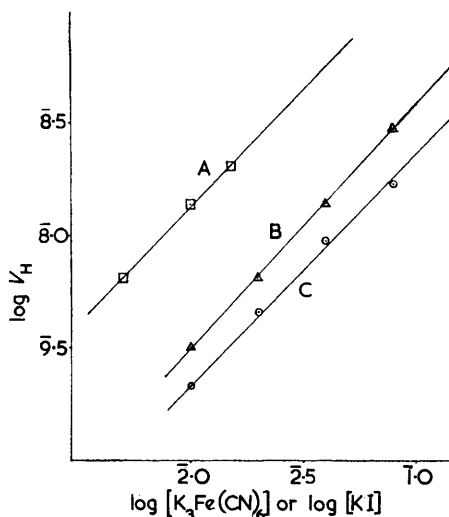


FIG. 2. Reaction orders in the catalysed reaction of ferricyanide with iodide ions.

- (A) Order with respect to $\text{Fe}(\text{CN})_6^{3-}$. (B) Order with respect to I^- , at $I = 0.15$. (C) Order with respect to I^- , at $I = 0.5$.

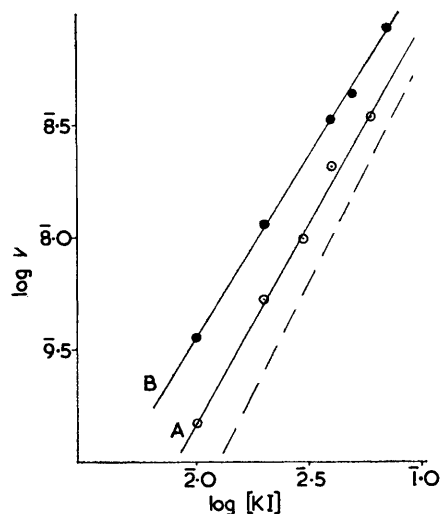


FIG. 3. Reaction orders with respect to I^- in the presence of $\text{La}(\text{NO}_3)_3$.

- (A) $[\text{La}(\text{NO}_3)_3] = 0.005$. (B) $[\text{La}(\text{NO}_3)_3] = 0.01$ mole l^{-1} . Broken line, slope 2.0.

Salt Effects on the Catalysed Reaction.—When the ionic strength increases from 0.15 to 0.50, the rate of the catalysed reaction increases much less than that of the uncatalysed reaction, as can be seen from Table 1. If the rate is given by:

$$-d[\text{Fe}(\text{CN})_6^{3-}]/dt = k[\text{Fe}(\text{CN})_6^{3-}][\text{I}^-]^2 + k_{\text{H}}[\text{H}^+][\text{Fe}(\text{CN})_6^{3-}][\text{I}^-],$$

the following values for k and k_{H} are obtained (k in $\text{l}^2 \text{mole}^{-2} \text{sec}^{-1}$):

$$\begin{array}{lll} I = 0.15; & k = 2.6 \times 10^{-4}; & k_{\text{H}} = 6.8 \times 10^{-3}. \\ I = 0.50; & k = 6.6 \times 10^{-4}; & k_{\text{H}} = 7.8 \times 10^{-3}. \end{array}$$

Reaction Order with Respect to Iodide in the Presence of La^{3+} ions.—Some runs were made with different concentrations of iodide in the presence of different concentrations of lanthanum nitrate. In these cases the rate cannot be conveniently considered as given by the sum of two terms, one independent of, and the other dependent on, the lanthanum-ion concentration, because of the uncertainty regarding the salt effects in the presence of multivalent cations.¹⁴

TABLE 4.

Reaction rates, $10^9 v$ (mole $\text{l}^{-1} \text{sec}^{-1}$), at different concentrations of KI and $\text{La}(\text{NO}_3)_3$ (mole l^{-1}) at 25°.

		$[\text{K}_3\text{Fe}(\text{CN})_6] = 0.01$ mole l^{-1} ; $I = 0.2$.						
$[\text{La}(\text{NO}_3)_3] = 0.005$	{ [KI] ...	0.01	0.02	0.03	0.04	0.06	} Order = 1.8	
	{ $10^9 v$	1.5	5.3	9.9	20.7	34.1		
$[\text{La}(\text{NO}_3)_3] = 0.01$	{ [KI] ...	0.01	0.02	0.04	0.05	0.07	} Order = 1.6	
	{ $10^9 v$	3.6	11.4	33.2	43.7	78.3		

¹⁴ Scatchard, Nat. Bur. Standards, Circular No. 524, 1953, p. 185.

Table 4 reports the results. For each lanthanum nitrate concentration the order with respect to iodide is also reported. Such orders have been calculated by minimizing the function:

$$\Sigma(\log k - a - n \log c)^2,$$

where c is the iodide concentration, a is a constant, and n is the reaction order. A bilogarithmic plot (Fig. 3) shows that the reaction order decreases with increasing La^{3+} concentration.

DISCUSSION

The accelerating effect of the hydrogen ion is so large that there is little doubt that there must be a short-range action on one of the reactants, or on both. In other words, it seems necessary to assume that the hydrogen ion is involved in the formation of the activated complex and that its effect is not limited to a purely electrostatic long-range action similar to normal salt effects. The absence of general acid catalysis excludes mechanisms involving slow transfer of a proton.¹⁵ The simplest interpretation is to assume that the H^+ ion is a part of the activated complex, which therefore should have the composition $[\text{HFe}(\text{CN})_6\text{I}]^{3-}$. Such an activated complex could be formed by interaction of the iodide ions with the $\text{HFe}(\text{CN})_6^{2-}$ ions, formed in a pre-equilibrium. The dissociation constant of $\text{HFe}(\text{CN})_6^{2-}$ is reported to be very large¹⁶ and is probably similar to that of the $\text{HP}_3\text{O}_9^{2-}$ ion, reported by Davies and Monk.¹⁷ Alternatively, the activated complex could be formed by a termolecular mechanism. The mechanism of formation is, however, irrelevant for our purposes, because the final result with respect to the kinetic parameters and the geometry of the activated complex is the same. Clearly the change in the ionic strength from 0.15 to 0.50 produces a change in rate constant k much larger than the change in k_{H} because of the smaller charge of the activated complex for the reaction path involving the hydrogen ion. Quantitative deductions are, however, almost impossible because of the high charge of one of the reactants and because of the high ionic strength. In these conditions the specific effects due both to the different ionic radii¹⁸ and to the change in the dielectric constant of the medium¹⁹ may completely outweigh the long-range interactions described by the Debye-Hückel limiting equations.

We think that the most interesting problem is the change in the reaction order with respect to iodide. This change might suggest a complete change in mechanism, but we do not think that such an assumption is necessary. Instead, we suggest for the uncatalysed reaction a mechanism somewhat different both from that postulated by Wagner¹ and from that of Bøchmann and Sandved.⁴ In fact, Wagner postulated the existence of an I_2^- ion merely on the basis of the second order with respect to iodide. We know of no other evidence for the existence of such an ion. Even for the iodide-iodate reaction, where, also, the order with respect to iodide is two,⁵ one need not assume an ion I_2^- , as has been shown by Morgan, Peard, and Cullis.²⁰ In our opinion, it is more reasonable to assume that the activated complex contains two iodide ions because of the greater stability of an eight-ligand co-ordination sphere than of a seven-ligand sphere in certain conditions. An example of this kind is given by the octacyanomolybdates and tungstates.²¹ At very low iodide concentrations the seven-ligand complex postulated by Bøchmann and Sandved⁴ becomes more stable for entropy reasons. The eight-ligand activated complex can easily dissociate into the $\text{Fe}(\text{CN})_6^{4-}$ ion, the I^- ion, and an atom of iodine. The independent existence of iodine atoms is well established, at least for the gaseous state.²² Later, the

¹⁵ Frost and Pearson, "Kinetics and Mechanism," Wiley and Sons, New York, 1953, p. 204.

¹⁶ Nekrasov and Zotov, *J. Appl. Chem. (U.S.S.R.)*, 1941, **14**, 264.

¹⁷ Davies and Monk, *J.*, 1949, 413.

¹⁸ Glasstone, "An Introduction to Electrochemistry," Van Nostrand Company, New York, 1942, p. 145.

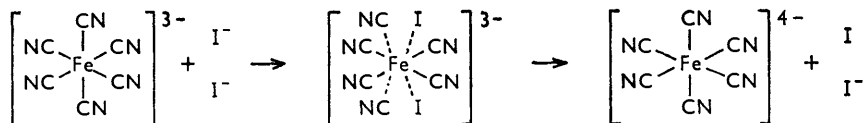
¹⁹ Hückel, *Phys. Z.*, 1925, **26**, 93; Bonino, *Gazzetta*, 1948, **78**, 61.

²⁰ Morgan, Peard, and Cullis, *J.*, 1951, 1865.

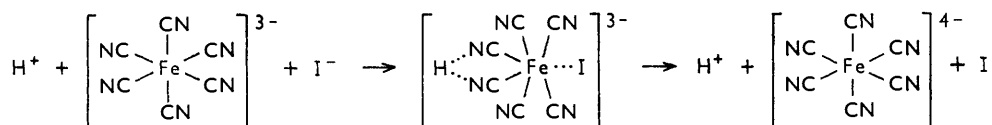
²¹ Basolo and Pearson, "Mechanisms of Inorganic Reactions," Wiley and Sons, New York, 1958, p. 398.

²² Moeller, "Inorganic Chemistry," Wiley and Sons, New York, 1952, p. 419.

iodine atoms can dimerize to I_2 and eventually form I_3^- . In conclusion, the uncatalysed reaction path could be rewritten as:



In the presence of the hydrogen ion, which strongly interacts with the CN^- groups, the geometry of the co-ordination sphere made up by these groups is considerably distorted because of the powerful polarizing action of the proton. In these conditions the stability of the sphere is decreased, and this is probably one of the reasons for the high acid strength of $\text{HFe}(\text{CN})_6^{2-}$. The presence of only one iodide ion may suffice to give to the co-ordination sphere stability sufficient to permit formation of the activated complex, so that it is no longer necessary to reach the co-ordination number eight. On the other hand, electron-transfer is rendered easier by the polarization of the electron cloud toward the proton, and this accounts for the catalysis. The catalysed reaction path, therefore, might be described as:



If this interpretation is correct, the hydrogen-ion catalysis of this reaction would not be fundamentally different from the non-electrostatic salt effects that have been detected and studied on several other occasions.²³ The main difference would lie in its extraordinary intensity which, in our opinion, is due to the fact that the hydrogen ion, in this case, can interact with the anion without participation of hydration water. In these conditions the charge density is enormous, owing to the very small radius of the proton. On the contrary, in other cases the proton cannot be freed from its water of hydration. Then the effect of the hydrogen ion is of the same order of magnitude as, or even smaller than, the effect of the alkali-metal ions.⁹ Another instance of interaction between the hydrogen ion and an anion without interposed water molecules is, probably, the hydration of the $\text{P}_3\text{O}_9^{3-}$ anion in acid medium.²⁴ A clear distinction between ion pairs with and without interposed water molecules has been recently made by Nancollas.²⁵

Because of the similarity between non-electrostatic salt effects and hydrogen-ion catalysis, a decrease of the reaction order with respect to iodide should be expected in the presence of other strongly polarizing cations. This prediction is borne out by the experiments reported in Table 4. Although, as we have said, it seems unsound to express quantitatively the rate in the presence of lanthanum ions as given by the sum of two terms, it is certain, however, that there is a strong association between La^{3+} and $\text{Fe}(\text{CN})_6^{3-}$. In fact, the dissociation constant of $\text{LaFe}(\text{CN})_6$ is $K = 1.82 \times 10^{-4}$ at 25° .²⁶ It is certain, also, that $\text{LaFe}(\text{CN})_6$ is a more reactive species than $\text{Fe}(\text{CN})_6^{3-}$ because of the decreased electrostatic repulsion, and this explains, at least partially, the catalytic effect of the lanthanum nitrate. Therefore, the rate expression takes the form:

$$\begin{aligned} \text{Rate} &= k[\text{Fe}(\text{CN})_6^{3-}][\text{I}^-]^2 + k'[\text{LaFe}(\text{CN})_6][\text{I}^-]^n \\ &= k[\text{Fe}(\text{CN})_6^{3-}][\text{I}^-]^2 + k'K^{-1}[\text{Fe}(\text{CN})_6^{3-}][\text{La}^{3+}][\text{I}^-]^n \end{aligned}$$

where, however, both k and k' vary in an unknown way with the La^{3+} concentration.¹⁴ If the order with respect to the iodide, n , in the second term were 2 the apparent order

²³ Indelli and Amis, *J. Amer. Chem. Soc.*, 1960, **82**, 332.

²⁴ Healy and Kilpatrick, *J. Amer. Chem. Soc.*, 1955, **77**, 5258.

²⁵ Nancollas, *Quart. Rev.*, 1960, **14**, 402.

²⁶ Davies and James, *Proc. Roy. Soc.*, 1948, *A*, **195**, 116.

with respect to the iodide would be 2 in all cases. The fact that experimentally a lower order is found, clearly indicates that n is less than 2 and is probably 1. As the lanthanum nitrate concentration is increased the relative importance of the second term increases, and therefore a lower apparent order with respect to iodide must be found. There seems little doubt that the presence of a lanthanum ion, with its high charge density, in the activated complex produces a non-electrostatic action, whether or not the increase in rate can be quantitatively accounted for by ion-pair formation. The fact that a decrease in the order with respect to iodide is found in the presence both of La^{3+} and of H^{+} seems to support the assumption of a substantial similarity between the catalyses in the two cases.

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