

## MECHANISTIC ASPECTS OF CHAIN INITIATION IN RADICAL ADDITION REACTIONS INDUCED BY METAL IONS

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Bersuker's concept of redox charge transfer in catalysis has been adopted to study initiating activity of metal ions in radical addition reactions of model organic addends with alkenes. It was found that the most important factor determining the activity of the metal ions was the magnitude of the redox charge transfer  $\Delta q$ . Additionally, the spin-allowedness or spin-forbiddenness of the redox step was essential. Two-valent metal ions with configurations  $d^5-d^9$  do not exhibit, regardless of the spin-allowedness of the redox step, a significant oxidation activity owing to low values of  $\Delta q$ . Three-valent metal ions with configurations  $d^1-d^3$  are also inactive because of relatively lowest values of  $\Delta q$  and spin-forbiddenness of the redox step. A transient position is occupied by the  $Mn^{3+}$  ( $d^4$ ) ion for which the redox step is still spin-forbidden, but the value of  $\Delta q$  is high enough to evoke satisfactory oxidation activity. Three-valent ions  $Fe^{3+}$ ,  $Ni^{3+}$  and  $Co^{3+}$  with configurations  $d^5-d^7$  as well as four-valent ions  $Pb^{4+}$  and  $Mn^{4+}$  show, according to the magnitude of  $\Delta q$ , the highest oxidation activity in chain initiation.

It is well documented experimentally that ketones, nitriles, esters, compounds with activated methylene group and some other organic addends readily add to alkenes in radical chain reactions initiated by thermal decomposition of organic peroxides. In such reactions, also the salts and oxides of transition metals in higher oxidation states can act as initiating agents. Synthetic features of the metal ion-initiated addition reactions have been relatively well established<sup>1-10</sup>. A few studies referring to the mechanism of these reactions<sup>3,11-14</sup> do not offer, however, an unambiguous interpretation of the detailed course, particularly of the chain initiation in these reactions. The mechanism proposed by Dewar and coworkers<sup>12</sup> involves in the first step the oxidation of an organic addend by a metal ion to form a radical cation; the formation of a radical cation is believed to not be the rate determining step. A transient existence of a radical cation was proved experimentally in the oxidation of substituted aromatic hydrocarbons and alkenes by manganese(III) and cobalt(III) acetates<sup>12,13,15-18</sup>. The radical cation once formed is stabilized in the next step by loss of a proton to form the corresponding radical which adds to an alkene in the propagation step of the reaction. Observed values of the primary kinetic isotopic effect  $k_H/k_D$  are in accordance with this mechanism<sup>11</sup>. The aspect which is still discussed is, above all, the nature of the oxidized species in cases where the organic addend may occur in several tautomeric forms. This is the case of ketones where both keto and enol form might participate in the reaction. A number of experimental results show that the rate of oxidation of acetone, methyl ethyl ketone and diethyl ketone is much faster than the rate of their enolization and the keto form is therefore believed to undergo oxidation<sup>11,19</sup>. On the other hand, preferential oxidation of the enol form is assumed by other authors. Thus, for example, Den Hartog and Kooyman<sup>20</sup>

found that the enolization is the rate determining step in the oxidation of acetophenone by cobalt(III) and manganese(III) acetates. The reaction of cyclohexanone with manganese(III) acetate is supposed to proceed *via* oxidation of the enol form<sup>14</sup>. Selective formation of 3-alkyl-2,4-pentanediones in the reaction of the easily enolizable 2,4-pentanedione with 1-alkenes initiated by silver(I) oxide has been explained by the preferential oxidation of the dione enol form<sup>21</sup>. In some cases, one cannot exclude a transient occurrence of metal enolates<sup>8,22</sup> provided that their formation is allowed by the reaction medium or by the acid-base properties of the initiating agent. No comparable kinetic data have been reported on the dependence of the rate of initiation step on the type of the corresponding metal ion and on the structure of oxidized addends.

In this work, an attempt has been made to estimate qualitatively the oxidizing activity of several metal ions and also the relative oxidation capability of organic addends in a series of model addition reactions. The estimation was based on the Bersuker's concept of redox charge transfer in catalysis<sup>23-25</sup>.

## RESULTS AND DISCUSSION

The experimental data available on the radical addition reactions are rather of a qualitative nature. To describe the chain initiating step, we have therefore decided to use, in the first approximation, the concept of redox charge transfer suggested by Bersuker<sup>23-25</sup>. According to this concept, the coordination of a substrate to an active site of a catalyst proceeds with levelling of the corresponding Fermi levels (ionisation potentials) and formation of common molecular orbitals of the substrate-catalyst complex. This levelling effect is accompanied by a charge transfer from the substrate to the catalyst and *vice versa*, in dependence on the relative position of Fermi levels for both components. Another factor decisive for determining the magnitude of the charge transfer  $q$  is the redox capacity of the catalyst  $C_i$ , in our case of the metal ion, and of the addend  $C_a$ , which is defined by the ratio of changes in the charge transfer  $\partial q$  to the changes in the Fermi level energy  $\partial \varepsilon$  (Eq. (1)).

$$C_j = \frac{\partial q_j}{\partial \varepsilon_j} \quad (1)$$

The magnitude of the charge transferred during coordination is given by the relation (2).

$$\Delta q = \frac{C_i \cdot C_a}{C_i + C_a} (\varepsilon_F^i - \varepsilon_F^a) \quad (2)$$

In addition to the numerical calculation based on Eq. (2), the magnitude of the charge transfer  $\Delta q$  can be determined also graphically, as shown in Fig. 1.

The values of  $\Delta q$ ,  $C_i$  and  $C_a$  so found represent a measure of the relative activities of both metal ions and oxidized model addends. In the first approximation, the

active species of the catalyst were considered to be free ions of the corresponding transition metals ( $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Mn}^{4+}$ ,  $\text{Pb}^{4+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Co}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Ni}^{3+}$ ,  $\text{V}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Ti}^{3+}$ ,  $\text{Cu}^{2+}$ ). The values of ionisation potentials necessary for the calculation of redox capacities for free ions were taken from Bersuker work<sup>26</sup>. Ionisation potentials of model addends in idealized geometries were calculated by a semiempirical INDO method, using the Koopmans theorem<sup>27</sup>. Ionisation potentials for the corresponding radical cations were calculated by using the UHF version of the INDO method.

Calculated  $C_i$  and  $C_a$  values are presented in Tables I and II. The redox capacities of individual metal ions are comparable within the framework of one order of magnitude and attain a rather small value. This agrees with the fact that, as to the oxidizing action of these ions, we do not deal here with a real catalytic effect but at last with a quantitative reduction of the ion. Similarly, small values of the  $C_a$  capacities demonstrate a relatively great resistance of the model addends toward oxidation. A more illustrative measure of the oxidizing capability is the magnitude of the charge  $\Delta q$  transferred in the redox step of a given reaction. The  $\Delta q$  values are summarized in Table III. From the data in this Table it is obvious that, according to the  $\Delta q$  value, the metal ions can be roughly divided into three groups, irrespective of the type of oxidized addends. Expectedly, the highest  $\Delta q$  values and thus also the highest redox activity were found for strong oxidizing ions,  $\text{Pb}^{4+}$  and  $\text{Mn}^{4+}$ . For two-valent ions, such as  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Fe}^{2+}$ , this quantity is smaller than one, with an exception concerning oxidation of the acetone enolate. The result shows that these two-valent ions are inactive in addend oxidations. The oxidation activity of ions of three-valent metals increases in the following sequence

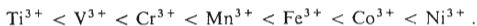
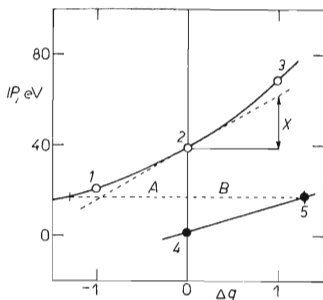


FIG. 1

Graphical Calculation of Redox Charge Transfer  $\Delta q$  in Reaction of Acetone Enolate with  $\text{Cu}^{2+}$  Ions

A  $\Delta q_{\text{red}}$ , B  $\Delta q_{\text{ox}}$ , 1  $\text{Cu}^{1+}$ , 2  $\text{Cu}^{2+}$ , 3  $\text{Cu}^{3+}$ ,  
4  $\text{CH}_2=\text{C}(\text{O}^-)-\text{CH}_3$ , 5  $\text{CH}_2=\text{C}(\text{O}^{\bullet})-\text{CH}_3$   
 $-\text{CH}_3 \longleftrightarrow \text{CH}_3\text{CO}\dot{\text{C}}\text{H}_2$ , X  $1/C_{\text{Cu}^{2+}}$ .



In this series, a transient position is occupied by the  $\text{Mn}^{3+}$  ion ( $d^4$ ) for which the redox step is still spin-forbidden (Table I), but the value of  $\Delta q$  (Table III) is high enough to evoke satisfactory oxidation activity<sup>1-5,11-15,28</sup>. The activity of the  $\text{Fe}^{3+}$  ion was established in the oxidation of enolizable ketones<sup>29</sup>. Unfortunately, there are no comparable data on the oxidation activity of  $\text{Fe}^{3+}$ ,  $\text{Co}^{3+}$  and  $\text{Ni}^{3+}$ .

TABLE I

Redox Capacities  $C_i$  For Metal Ions ( $\text{M}^{n+}$ ) Calculated According to Eq. (I)

$\text{M}^{n+}$	Con- figuration	Spin-allowedness (A) and -forbiddenness (F)	$C_i \cdot 10^6$ $\text{cm}^{-1}$	$C_i$ $\text{eV}^{-1}$	$C_i \cdot 10^4$ $\text{kJ}^{-1} \text{mol}$
$\text{Mn}^{2+}$	$d^5$	A	7.288	0.0588	6.093
$\text{Fe}^{2+}$	$d^6$	A	7.072	0.0570	5.907
$\text{Co}^{2+}$	$d^7$	A	6.823	0.0503	5.212
$\text{Ni}^{2+}$	$d^8$	A	6.566	0.0529	5.482
$\text{Cu}^{2+}$	$d^9$	A	6.173	0.0498	5.161
$\text{Ti}^{3+}$	$d^1$	F	6.107	0.0492	5.098
$\text{V}^{3+}$	$d^2$	F	6.142	0.0495	5.129
$\text{Cr}^{3+}$	$d^3$	F	6.125	0.0494	5.119
$\text{Mn}^{3+}$	$d^4$	F	6.046	0.0487	5.047
$\text{Fe}^{3+}$	$d^5$	A	5.917	0.0477	4.943
$\text{Co}^{3+}$	$d^6$	A	5.737	0.0463	4.798
$\text{Ni}^{3+}$	$d^7$	A	5.534	0.0446	4.622
$\text{Mn}^{4+}$	$d^3$	F	5.165	0.0416	4.311
$\text{Pb}^{4+}$	$d^{10}$	A	7.202	0.0581	6.021

TABLE II

Redox Capacities  $C_a$  For Organic Model Addends Calculated According to Eq. (I)

Addend	$C_a \cdot 10^5$ $\text{cm}^{-1}$	$C_a$ $\text{eV}^{-1}$	$C_a \cdot 10^7$ $\text{kJ}^{-1} \text{mol}$
Acetone	1.089	0.0878	8.788
Acetone enol	1.212	0.0977	10.120
Acetone enolate	1.031	0.0832	8.622
2,4-Pentanedione	3.179	0.2564	26.570
Acetonitrile	1.243	0.1003	10.390

ions; according to our estimation,  $\text{Fe}^{3+}$  and  $\text{Co}^{3+}$  ions would be more active than  $\text{Mn}^{3+}$  ions. Expectedly,  $\text{Cr}^{3+}$  ions are inactive in the initiation of addition reactions<sup>8</sup>. The reason for their inactivity can be sought for both in the relatively lowest  $\Delta q$  values and, above all, in the spin-forbiddenness of the redox step.

The mechanism of redox initiation suggested by Dewar<sup>12</sup> implies that the charge transfer is not the rate determining step (Eqs (A) and (B)).



On the basis of the correlation diagrams one can demonstrate that for ions with configuration  $d^1 - d^4$  the spin ground state of the addend ... ion complex correlates directly with the excited state of the complex radical-cation ... reduced ion. For example, the ground state of the ion with configuration  $d^1$  ( $\text{Ti}^{3+}$ ) is given by the term  $^2D$  while for the corresponding reduced form ( $d^2, \text{Ti}^{2+}$ ) the term for the ground

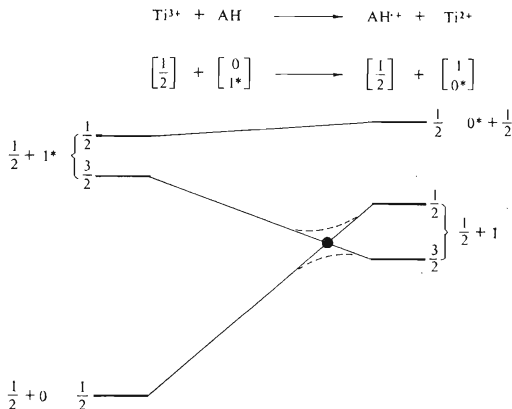
TABLE III

Values of Redox Charge Transfer  $\Delta q$  For Series of Metal Ions ( $\text{M}^{n+}$ ) and Organic Model Addends Calculated According to Eq. (2)

$\text{M}^{n+}$	Acetone	Acetone enolate	Acetonitrile	2,4-Pentanedione	Acetone enol
$\text{Mn}^{2+}$	0.66	1.05	0.67	0.94	0.75
$\text{Co}^{2+}$	0.70	1.06	0.70	0.96	0.78
$\text{Ni}^{2+}$	0.78	1.14	0.79	1.07	0.86
$\text{Fe}^{2+}$	0.70	1.08	0.71	0.99	0.79
$\text{Ti}^{3+}$	1.01	1.36	1.03	1.36	1.10
$\text{V}^{3+}$	1.07	1.42	1.09	1.44	1.17
$\text{Cr}^{3+}$	1.12	1.46	1.14	1.47	1.21
$\text{Mn}^{3+}$	1.18	1.52	1.21	1.57	1.28
$\text{Fe}^{3+}$	1.23	1.56	1.26	1.64	1.35
$\text{Co}^{3+}$	1.27	1.60	1.31	1.68	1.37
$\text{Ni}^{3+}$	1.31	1.63	1.35	1.72	1.41
$\text{Mn}^{4+}$	1.70	1.99	1.74	2.18	1.80
$\text{Pb}^{4+}$	1.81	2.17	1.87	2.49	1.94
$\text{Cu}^{2+a}$	0.80	1.37	0.82	1.25	0.95

<sup>a</sup> The  $\Delta q$  values were determined graphically (Fig. 1).

state is  $^3F$ . As the ground state configuration of the oxidized addend is a singlet and the lowest excited state configuration is a triplet, one can construct, using the rule of addition of spin-impuls moments, the correlation diagram visualized by Scheme 1. Due to the spin-orbital interaction, the ground state of the starting components correlates finally with the ground state of products. However, the "intended crossing" of the corresponding potential hypersurfaces will manifest itself as an energetic



SCHEME 1

barrier causing a slow-down or even forbiddenness of the redox step. From the data in Table I it is clearly seen that starting from the  $d^5$  configuration the redox step of the reaction is spin-allowed and takes place therefore without energetic demands. On the basis of these results one can modify the original initiation mechanism proposed by Andrulis<sup>12</sup> in that the assumption about the initial fast oxidation step forming a radical cation holds for ions with configurations  $d^5 - d^9$ , while for ions with configurations  $d^1 - d^3$  or even  $d^1 - d^4$  the rate of addend oxidation appears to be comparable with that of deprotonation of the radical cation.

Further conclusions interesting from the mechanistic point of view can be drawn from the values of  $\Delta q$  for a series of different organic model addends. From Eq. (2) one can see that, with respect to the nearly identical values of the redox capacities  $C_i$  for metal ions, the differences in  $\Delta q$  for individual addends are due predominantly to the differences in the capability of these addends to undergo ionisation. The oxidation of acetone and of its enol form shows that due to the lower ionisation potential,

the enol form is oxidized more easily. Still easier will be the oxidation of the corresponding enolate ion; in this case, even the oxidizing capability of the  $\text{Cu}^{2+}$  ions is large enough to induce a rapid addend oxidation (Table I).

On the basis of  $\Delta q$  values (Table III) one can arrive at the following order of oxidation capability of model addends: acetone enolate > acetone enol > acetone; 2,4-pentanedione < acetone; acetone  $\sim$  acetonitrile<sup>6,8-10</sup>. Presumably because of spin-forbiddenness for ions with configuration  $d^1 - d^3$  or even  $d^1 - d^4$ , the rate of oxidation of an addend is comparable with that of the subsequent deprotonation of a transiently formed radical cation.

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