

## Kinetics & Mechanism of Oxidation of Toluenes by Lead Tetraacetate

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Kinetics of oxidation of toluene, *p*-xylene, *p*-methoxytoluene, diphenylmethane (DPM), triphenylmethane (TPM) and fluorene by lead tetraacetate (LTA) in acetic acid/sodium acetate at 80° have been investigated. The products are exclusively the corresponding side chain mono-acetoxyated derivatives. There is a second order dependence on [substrate] in the case of toluene and substituted toluenes whereas the order with respect to DPM, TPM and fluorene is one. The kinetic order with respect to LTA is one for all the compounds studied. A change in the solvent system has a significant effect on the oxidation rate of the various substrates, and the rate decreases in the order: HOAc/DMF > HOAc > HOAc/DMSO > HOAc/CH<sub>3</sub>CN ~ HOAc/cyclohexane > HOAc/CH<sub>2</sub>Cl<sub>2</sub> ~ HOAc/nitrobenzene > HOAc/benzene. Cl<sup>-</sup> and Mn<sup>2+</sup> ions catalyse the oxidation, whereas addition of water in small amounts does not affect the rate. Reactions carried out in pure propionic acid show rate enhancement. Positive acid catalysis has been observed in the oxidation of fluorene which is traced to the specific labile nature of the substrate in acid medium.

AS a part of our scheme on the kinetics of oxidation of hydrocarbons by various oxidants<sup>1a-c</sup>, it was thought of interest to study the kinetics of oxidation of toluene, *p*-xylene and *p*-methoxytoluene, diphenylmethane (DPM), triphenylmethane (TPM) and fluorene by lead tetraacetate (LTA) in acetic acid and in binary mixtures of HOAc/DMF, HOAc/benzene, HOAc/nitrobenzene, HOAc/CH<sub>3</sub>CN, HOAc/DMSO, HOAc/cyclohexane and HOAc/methylene chloride. The results of these investigations are presented in this paper.

### Materials and Methods

Lead tetraacetate (K. Light, AR) of 97% purity was stored in a desiccator under vacuum. The LTA solutions were found to be stable under the various conditions used. Acetic acid (AR, BDH) was purified as usual. Conductivity water was used throughout. Toluene, *p*-xylene, *p*-methoxytoluene, DPM, TPM and fluorene were all BDH (AR) grade chemicals and were redistilled or recrystallized before use.

The decomposition of LTA in acetic acid/NaOAc has been the subject of a number of investigations<sup>2,3</sup> and no definite integral order kinetics was observed, but the decomposition of LTA could be retarded by Pb(OAc)<sub>2</sub>. Under the present conditions the loss of Pb(OAc)<sub>4</sub> due to self-decomposition in HOAc/NaOAc was not more than 6% in a given kinetic run. Even in HOAc/water (95:5, v/v), LTA was quite stable.

Five ml aliquots from the reaction mixture and also from the blank were withdrawn at various intervals and added to 10 ml of 5% KI and excess of sodium acetate. The liberated iodine was titrated against the standardized thiosulphate solution. All the experiments were performed in duplicate and were reproducible within ±5%.

### Results and Discussion

The rate expression for the oxidation of substituted toluenes by LTA is given by Eq. (1).

$$-\frac{d[\text{Pb(IV)}]}{dt} = k[\text{Toluene}]^2[\text{LTA}] \quad \dots(1)$$

The plots of log *k*<sub>1</sub> versus log [S] were linear with slope = 2.0, thereby showing the order with respect to substrate to be two. This is the first report on the second order dependence with respect to hydrocarbon in hydrocarbon oxidations by any metal ion oxidant. The order with respect to LTA is one as seen by the linear plots of log (a-x) versus time. However, in the case of DPM, TPM and fluorene the order with respect to both substrate and LTA is one. The results are given in Tables 1 and 2. The differences in the order with respect to substrate may be attributed to the differences in structure and geometry of the molecules.

It is seen that electron releasing groups favour the reaction (Table 3). As for example *p*-methoxytoluene and TPM are oxidized at a much faster rate as compared to other substrates. The abnormal behaviour of fluorene can be traced to difficulty in approach by the oxidants LTA (being comparatively bulky) to the fused ring system of fluorene.

The plots of log *k*<sub>1</sub> versus σ or σ\* (Hammett and Taft substituent constant respectively)<sup>4</sup> are linear with ρ = -2.5, indicating that the reaction takes place through radicals with slight cationic nature. Such ρ values have been reported in the oxidation of diphenylmethanols<sup>5</sup> by Ce(IV), in the decarboxylation of phenylacetic acids<sup>6</sup> by Ce(IV), and in oxidation of hydrocarbons<sup>7-9</sup> by Mn<sup>3+</sup>, Co<sup>3+</sup> and MnO<sub>4</sub><sup>-</sup>.

Small percentages of water have been found to catalyse diol cleavage<sup>10</sup> by LTA and the reaction of anthracene<sup>11</sup> by LTA. In the present investigation the rates remained almost unaffected by the

TABLE 1 — EFFECT OF VARYING [SUBSTRATE] ON THE OXIDATION OF TOLUENE AND SUBSTITUTED TOLUENES BY LTA AT 80°C

[Solvent = 100% acetic acid, [NaOAc] = 0.02M,  
[Pb(IV)] = 0.0075M}

[Substrate] M		$10^5 k_1$ (min <sup>-1</sup> )
	TOLUENE	
0.351		12.76
0.312		8.71
0.221		5.3
0.1634		3.1
0.087		1.25
	<i>p</i> -XYLENE	
0.21		45.87
0.1908		35.24
0.14		19.0
0.10		8.1
0.04958		4.5
	<i>p</i> -METHOXYTOLUENE	
0.3188		95.0
0.25		80.0
0.1975		47.0
0.099		15.0

TABLE 2 — EFFECT OF VARYING [SUBSTRATE] ON THE OXIDATION OF DPM, TPM AND FLUORENE BY LTA AT 80°C IN ACETIC ACID

{[Pb(IV)] = 0.0075M; [NaOAc] = 0.02M}

[Substrate] M	$10^4 k_1$ (min <sup>-1</sup> )	$k_2$ (litre mole <sup>-1</sup> min <sup>-1</sup> )
	TRIPHENYLMETHANE	
0.04346	56.61	0.130
0.01170	14.62	0.125
0.006549	8.187	0.125
	DIPHENYLMETHANE	
0.09774	11.00	0.0110
0.07415	8.0	0.0108
0.02580	2.58	0.0100
	FLUORENE	
0.1016	103.5	0.103
0.07820	82.0	0.104
0.04814	46.1	0.09568

TABLE 3 — REACTIVITY ORDER IN THE OXIDATION OF COMPOUNDS BY LTA AT 80°C

{Solvent = 100% HOAc; [substrate] = 0.1M;  
[Pb(IV)] = 0.0075M; [NaOAc] = 0.02M}

Compound	$10^5 k_1$ (min <sup>-1</sup> )	Substituent constant
Toluene	1.4	0.00
<i>p</i> -Xylene	8.1	-0.17
<i>p</i> -Methoxytoluene	15.0	-0.268
Diphenylmethane	110.0	-0.68*
Triphenylmethane	1300.0	-1.02*

\*Computed values of Taft substituent constants<sup>4</sup>.

TABLE 4 — EFFECT OF ADDING ORGANIC SOLVENTS ON THE SECOND ORDER RATE CONSTANTS OF FLUORENE AND TPM AT 80°C

{[Pb(IV)] = 0.0075M; [substrate] = 0.0240M;  
[NaOAc] = 0.02M}

Solvent*	$k_2$ (litre mole <sup>-1</sup> min <sup>-1</sup> )	
	Fluorene	TPM
5% DMF	0.2475	0.45
10% DMF	0.75	1.12
5% benzene	0.053	0.076
10% benzene	0.050	0.073
15% benzene	0.042	0.068
5% nitrobenzene	0.058	0.084
10% nitrobenzene	0.051	0.081
5% DMSO	0.087	—
5% CH <sub>2</sub> Cl <sub>2</sub>	0.053	0.080
5% CH <sub>3</sub> CN	0.075	—
5% Cyclohexane	0.077	—

\*Percentage (v/v) of other organic component in HOAc is given.

TABLE 5 — EFFECT OF ADDED SALTS ON THE OXIDATION OF FLUORENE BY LTA

{Solvent = HOAc/water (95:5, v/v); [Pb(IV)] = 0.007M;  
[substrate] = 0.024M; [salt] = 0.002M}

Salt	$k_2$ (litre mole <sup>-1</sup> min <sup>-1</sup> )	Salt	$k_2$ (litre mole <sup>-1</sup> min <sup>-1</sup> )
Pb(OAc) <sub>2</sub>	0.1150	Uranyl acetate	0.12
Mg(OAc) <sub>2</sub>	0.10	Ca(NO <sub>3</sub> ) <sub>2</sub>	0.10
Ca(OAc) <sub>2</sub>	0.12	CaCl <sub>2</sub>	0.92

addition of water. It is pertinent to remark that LTA solutions are quite stable in acetic acid/water (95:5%, v/v).

The acceleration by added water in systems like anthracene<sup>10</sup> has been attributed to the addition reaction, and in systems like glycols<sup>11</sup>, it has been suggested that it might be due to exchange of acetate by water molecules in the solvation sphere. Since the effect of added water is negligible, none of the above postulates holds good in the present systems.

A change in the solvent system has a significant effect on the oxidation rate of the various substrates. The reactions are comparatively faster in HOAc/DMF mixtures (Table 4). The order of reactivity is: HOAc/DMF > HOAc > HOAc/DMSO > HOAc/CH<sub>3</sub>CN ~ HOAc/cyclohexane > HOAc/CH<sub>2</sub>Cl<sub>2</sub> ~

HOAc/NO<sub>2</sub>-benzene ~ HOAc/benzene. In general the reactions are retarded by the addition of organic solvents to HOAc except when DMF is added. The rate acceleration in DMF is not unknown. The plots of log  $k_2$  versus  $1/D$  ( $D$  = dielectric constant) in each solvent system are linear thereby showing that within the same binary solvent mixture the dielectric effect operates in the process. This clearly indicates that these reactions are of dipole-dipole type.

Because of solubility limitations, HOAc/water (95:5, v/v) was used as the ideal solvent composition for studying salt effects. Pb(OAc)<sub>2</sub>, a product in LTA oxidation, does not retard the reaction. The effect of other salts is only slight (Table 5), confirming the reactions to be of dipole-dipole type.

TABLE 6 — EFFECT OF ADDING HClO<sub>4</sub>

[Solvent = 100% acetic acid; [HClO<sub>4</sub>] = 0.05M;  
[substrate] = 0.02M; [Pb(IV)] = 0.01M]

Compound	$k_2$ (litre mole <sup>-1</sup> min <sup>-1</sup> )	$k_2$ (litre mole <sup>-1</sup> min <sup>-1</sup> )*
DPM	10.008	0.0099
TPM	0.14	0.13
Fluorene	4.4	0.10

\*In the presence of HOAc/NaOAc without HClO<sub>4</sub>.

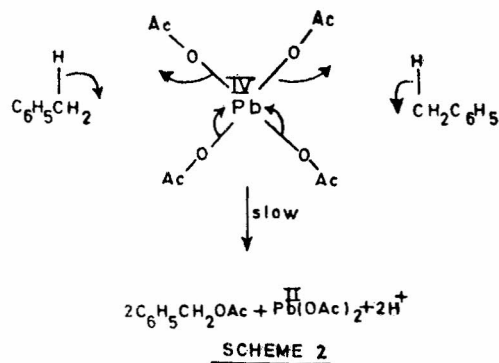
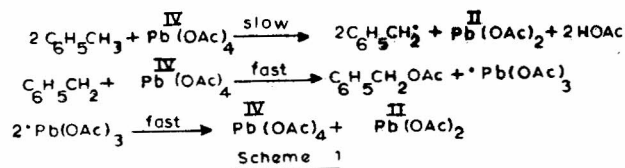
The acceleration observed in the presence of Cl<sup>-</sup> deserves some comment. The oxidation in the presence of Cl<sup>-</sup> proceeds through the same electron transfer mechanism as in the absence of Cl<sup>-</sup>. It seems probable that the major influence of added Cl<sup>-</sup> is to render Pb(IV) a stronger oxidizing agent, as it has been found in the Co(III) oxidation of toluenes (loc. cit) in the presence of LiCl. Cl<sup>-</sup> ion catalysis has been observed earlier in the halodecarboxylation of acids by LTA<sup>12</sup> in the presence of CaCl<sub>2</sub> and LiCl.

Added Mn<sup>2+</sup> accelerates the oxidation of fluorene by LTA. Mn<sup>2+</sup> causes an acceleration as its effect is not only due to its ionic strength but it is an oxidizable ion as well. The values of  $k_2$  for the oxidation of fluorene at 80° are 0.080, 0.165 and 0.289 at [Mn<sup>2+</sup>] = 0.00, 0.0002980 and 0.001078M respectively in acetic acid/water (95:5, v/v) using [fluorene] = 0.024M, [Pb(IV)] = 0.0070M, and [NaOAc] = 0.02M.

It has been observed that there is a two-fold acceleration in 100% propionic acid, compared to HOAc [ $k_2 = 0.173$  for fluorene and 0.33 for TPM in 100% propionic acid at 80°]. This seems to point out that solvent participation is unlikely, as in esterification reactions acetic acid functions better and faster than propionic acid. If at all the propionic acid participates in the reaction to give the observed rate enhancement, it is indirect and presumably through the exchange of acetate by propionate as claimed by Davies<sup>13</sup> in the synthetic work on toluene in propionic acid where benzyl propionate was the major product in addition to benzyl acetate.

It has been observed that addition of HClO<sub>4</sub> has no effect on the rates of oxidation of DPM and TPM (Table 6). This rules out that there is any change in the oxidizing species as postulated by Ouellette *et al.*<sup>14</sup>. If it is due to a change in the oxidizing species by the addition of HClO<sub>4</sub> the effect would have been uniform and general. The abnormal acceleration in the case of fluorene by the addition of HClO<sub>4</sub> may be attributed to the specific acid catalysis and not to the species Pb(OAc)<sub>3</sub><sup>+</sup>ClO<sub>4</sub><sup>-</sup>. The positive acid catalysis is significant as the acceleration outweighs the retardation due to steric factor in the absence of HClO<sub>4</sub>.

**Mechanism of oxidation of toluene and substituted toluenes** — Toluene reacted at 80° to give exclusively benzyl acetate. Neither nuclear acetoxylation nor nuclear methylated products were detected.



In conformity with the second order dependence on toluene and substituted toluenes and first order dependence on LTA the Schemes 1 and 2 have been proposed.

The dimerization of benzyl radical is ruled out as there is no dibenzyl produced and therefore the radicals are short-lived and they collide with LTA giving benzyl acetate and lead triacetate radical. The latter would start a new chain or disproportionate to LTA and Pb(OAc)<sub>2</sub>.

Alternatively it could be by a concerted process (Scheme 2) without the intermediacy of a benzyl radical.

Both the pathways are consistent with experimental observations and it is difficult to choose between them, though the second alternative is generally preferred by many workers<sup>13,15,16</sup> in their synthetic work on toluenes with LTA.

**Mechanism of oxidation of DPM, TPM and fluorene** — The reaction pathway for these compounds is much simpler as the kinetic dependence is first order with respect to each LTA and the substrate. Hence a hydrocarbon molecule reacts with a mole of Pb(IV) forming a short-lived radical or by a concerted mechanism leading to the corresponding acetoxy derivative.

The electrophilic substitution postulated for nuclear acetoxylation is unlikely under the present experimental conditions as the products isolated are the side chain acetoxylation derivatives.

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