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The Recation of Lead Tetracetate with Anethole
Addition Equilibria and Kinetics[a]

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It has been shown that the reaction of lead tetraacetate with anethole to form diacetox-yanethole in acetic acid proceeds through a formation of an addition compound. The con-centrations of the adduct are determined by an equilbrium equation : Anethole + lead tetra-acetate ⇌ adduct. For the first time, such an equilibrium between an olefinic compound and lead tetraacetate has been demonstrated.

The rates of the formation of the final product are first-order with respect to the adduct. The reaction proceeds faster in the solvents with stronger ionizing power.

The reaction of lead tetraacetate with olefinic compounds to form diacetoxy compounds is one of the typical reactions of this reagent with organic compounds[1]. To make clear this mechanism, the kinetics of the reaction with anethole has been studied by following the decreases of the lead tetraacetate concentrations iodome-trically, since this reaction proceeds without appreciable side reactions under the conditions convenient to the kinetic study.

$$CH_3OC_6H_4CH{=}CHCH_3 + Pb(OAc)_4 \xrightarrow{HOAc} CH_3OC_6H_4CH{-}CH{-}CH_3 + Pb(OAc)_2$$
$$\underset{OAc\ OAc}{\qquad}$$
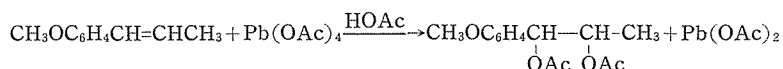
This equation has been established by Dimroth[2] and Criegee[3]. During the course of the experiments to check their results, it was confirmed that no ga-seous products were formed in contrast to the other cases such as those in the oxidations of monohydric alcohols and triphenylmethane by the same reagent[4]. It was also observed that a yellow color developed instantly when anethole was added to lead tetraacetate in acetic acid. This color remained unchanged until no more lead tetraacetate could be detected by iodometry. The same color was observed in the case of benzene solution too. However, no definite absorption max-imum was detected in visible and near u. v. regions by spectrophotometric meth-od, where both the reactants and the products are transparent.

When the acetic acid solutions of lead tetraacetate were added to those of anethole, the concentrations of the former (determined iodometrically) decreased instantly. The extents of the decreases depend on the concentrations of both reactants and are not affected by the presence of sodium acetate (0.1 molar). After these instant drops, the oxidant concentrations decreased slowly as usual.

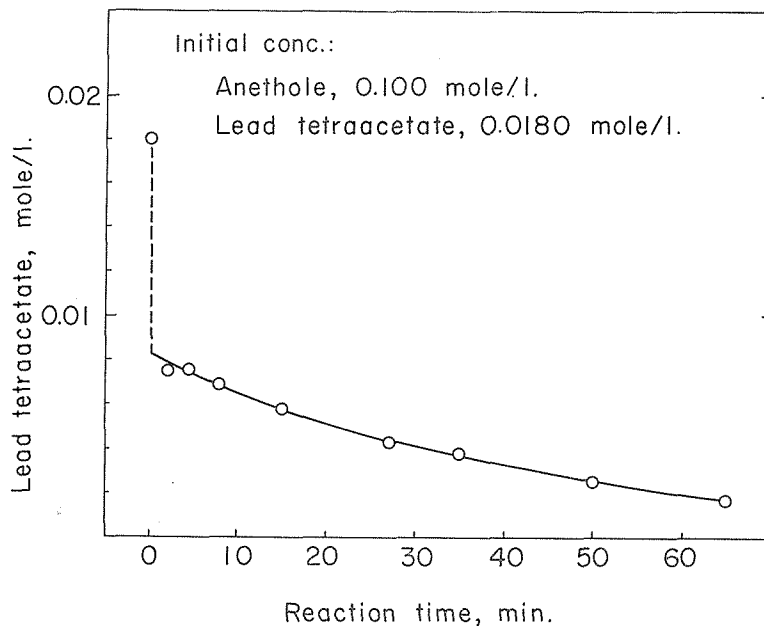Katsuhiko ICHIKAWA, Yoshiichi TAKEUCHI and Osamu ITOH

Fig. 1. A typical example of time-lead tetraacetate concentration
curve of the reaction between lead tetraacetate and anethole
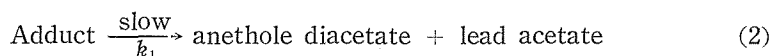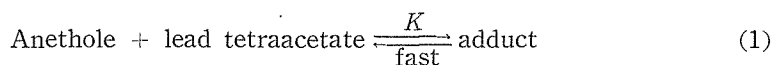in glacial acetic acid at 30.0°.

A typical example is shown in Fig. 1.

These observations, together with the color development of the reaction mix-
tures mentioned above, indicate strongly a formation of some sort of addition
compound. Data suggest that an addition equilibrium exists and is attained fast.
Assuming that the initial decreases of the lead tetraacetate concentrations (esti-
mated by extrapolations of the time-concentration curves and shown in Fig. 2.)
are proportional to the concentrations of the adduct, several attempts to calculate
the equilibrium constant have been carried out.

However, the behavior of the adduct toward potassium iodide solution in iodo-
mery is not clear. Because the titers of the reaction mixtures at time 0 decrease,
the oxidation equivalent of lead tetraacetate (2-electron unit oxidant) should have
been decreased by forming the adduct. If it is assumed that the adduct acts as
a one-electron unit oxidant toward potassium iodide solution, its concentrations
exceed those of the initial lead tetraacetate in many cases. Therefore, the adduct
can not be an oxidant.

On the assumption mentioned above, the decreases of the lead tetraacetate
concentrations from the initial ones at time t correspond to $C_t + x$, where C_t and
x are the concentrations of the adduct and the product formed at time t respect-
ively.

If the reaction proceeds through the following mechanism (Eq. 1 and 2),

$$\text{Anethole} + \text{lead tetraacetate} \underset{\text{fast}}{\overset{K}{\rightleftharpoons}} \text{adduct} \tag{1}$$

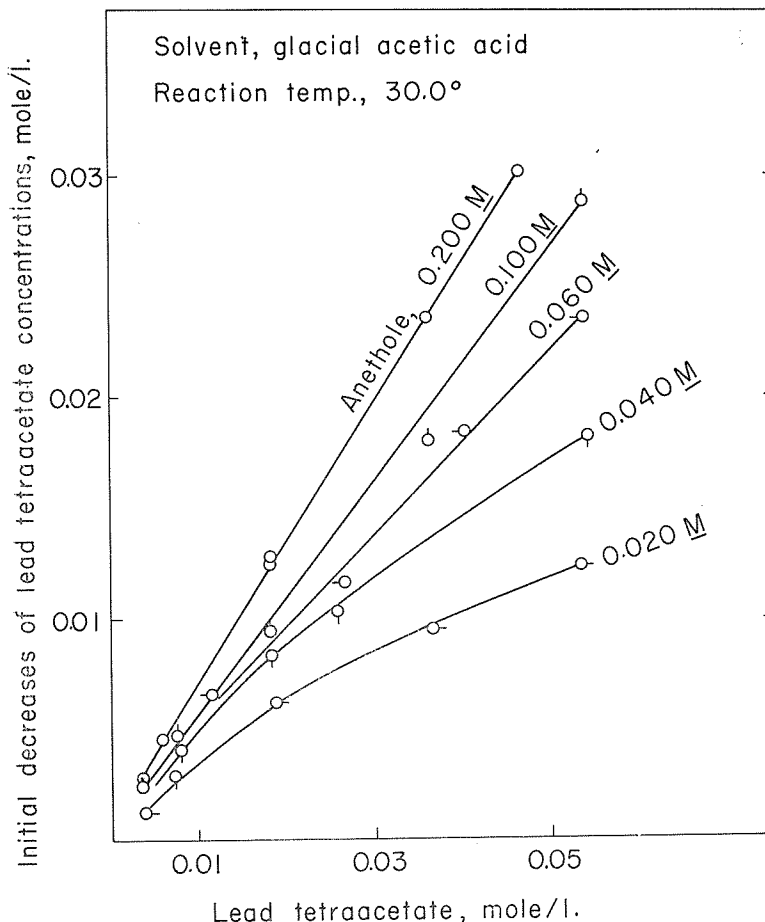$$\text{Adduct} \xrightarrow[k_1]{\text{slow}} \text{anethole diacetate} + \text{lead acetate} \tag{2}$$

Fig. 2. Effects of the initial concentrations of the ractants on the
initial decreases of the lead tetraacetate concentrations.

the rate of decrease of the lead tetraacetate after the initial drops can be expressed by Equation 3.

$$-d[Pb(OAc)_4]/dt = k_1[\text{adduct}] = k_1K(A_0-C_t-x)(B_0-C_t-x) \qquad (3)$$

A_0 and B_0 are the initial concentrations of anethole and lead tetraacetate respectively.

Introducing experimental data for C_t-x into equation 3, the values of k_1K have been calculated and shown in Table 1. In the wide range of the reactants concentrations, these values are constant. In each kinetic run, the second-order plots gave straight lines passing through the origin up to more than 80% decrease of lead tetraacetate. These support the assumptions mentioned above.

The values of K can be calculated from the initial drops of the lead tetraacetate concentrations at time 0, being shown in Table 1 together with k_1K values. With lower concentrations of anethole, fairly good constant values have been obtained in the concentration range of 0.0075-0.054 molar lead tetraacetate, but these are much smaller with higher anethole concentrations. It does not appear, however, that this is due to the incorrect assumptions. The deviations seem to

Table 1. Addition equilibria and rate data for the reaction of lead tetraacetate with anethole in glacial acetic acid at 30°.

Initial conc. of		$k_1K \times 10^3$ 1/mole. sec.	K
anethole mole/1	lead tetraacetate mole/1		
0.0200	0.00753	—	37
	.0188	5.2	36
	.0366	4.0	36
	.0536	4.3	39
.0400	.00359	—	31
	.00722	—	33
	.0179	5.7	27
	.0252	5.5	24
	.0400	5.5	22
	.0538	—	24
.0060	.0114	4.5	25
	.0267	4.8	16
	.0400	5.2	21
	.0537	5.0	16
.100	.0036	—	20
	.0072	—	20
	.0180	4.8	12
	.0360	6.0	12
	.0539	4.5	16
.200	.00619	—	14
	.0180	5.2	13
	.0356	5.7	13
	.0467	5.3	11

have resulted from the following two reasons. In the case of higher anethole concentrations, the rates of decreases of the oxidant are so great that the extrapolations of the time-concentration curves to time 0 are difficult. It is assumed that the equilibrium 1 is attained very fast, but the rates could not be great enough to determine the correct K values at time O. Both of these should have resulted in the smaller K values. It is concluded, therefore, that the most probable K value is the largest one, i. e., 36–39.

The experimental results are far from sufficient to discuss the structure and properties of the adduct and the mechanism of Equation 2. However, the fact mentioned below might throw a light on these points. The rate is much faster in 95% acetic acid than in glacial acetic acid by a factor of more than 10 and very slow in benzene solution containing 2% acetic acid. It is clear, therefore, that the reaction is faster in the solvent with higher dielectric constant and re-action 2 involves an ionic character. This appears also to be the reason why the adduct is not an oxidant for aqueous patassium iodide solution, since reaction 2 of the adduct will proceed very rapidly in the stop solution of the kinetic measurement.

EXPERIMENTAL

Materials. Commercial anethole was distilled twice before use, b. p. 105–107° at 12.5 mmHg, $n^{25}{}_D = 1.5590$. Acetic acid was used after a distillation through a packed column, b. p. 117–118° at 760 mmHg. Lead tetraacetate was prepared by the usual method[5] and used after a recrystallization from acetic acid. The other reagents were the commercial products of analytical grade.

Optical measurements. Adsorption spectra were determined by Beckman DU type spectrophotometer at room temperature.

Reaction of Lead Tetraacetate with Anethole:

Kinetic measurements. Solutions of anethole in acetic acid were added to solutions of lead tetraacetate in the same solvent under vigorus stirring. At proper intervals, aliquots (10 ml) were withdrawn and added to 25 ml of stop solution (one 1 of the solution contains 50g of KI, 100g of Na_2CO_3, 300g of NaOAc. $3H_2O$ and water). The liberated iodine was titrated with $0.05N$ sodium thiosulfate.

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