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On the Mechanism and Substituent Effects of the Tl(III) Oxidation of Phenylethylenes in Methanol

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The oxidation of phenylethylenes by Tl(NO₃)₃ in methanol proceeds rapidly and selectively to give the products resulting from the migration of aryl groups, *i.e.*, (*i*) the 1,1-dimethoxy-2-phenylethanes from the corresponding styrenes, (*ii*) the phenylacetones from the α -methylstyrenes, and (*iii*) the two possible deoxybenzoines from the 1,1,-diphenylethylenes. The kinetic results, which indicate the formation of the thallic-organic intermediate to be the rate determining step, are discussed in terms of the mechanism of reaction and show the role of the coordination of Tl(III). Hammett's relationship, with $\rho = -4.2$, describes the substituent effects for the competitive oxidation of ring-substituted styrenes and α -methylstyrenes. The relative migratory aptitudes of aryl groups, as determined from the oxidation products of ring-substituted 1,1-diphenylethylenes, is correlated to Brown's σ^+ constants, with $\rho^+ = -2.27$.

L'oxydation des phényléthylènes par le nitrate thallique dans le méthanol conduit rapidement et de manière sélective aux produits résultant de la migration des groupes aryles, c.à.d. (*i*) les diméthoxy-1,1 phényl-2 éthanes à partir des styrènes correspondants, (*ii*) les phénylacétones à partir des α -méthylstyrènes, et (*iii*) les deux désoxybenzoïnes possibles à partir de diphenyl-1,1 éthylènes. Les résultats cinétiques, qui indiquent que la formation de l'intermédiaire organo-thallique constitue l'étape déterminante, sont discutés en termes mécanistiques et, de plus, illustrent le rôle de l'état de coordination du Tl(III). La relation de Hammett, avec $\rho = -4.2$, décrit l'effet de substituants dans l'oxydation compétitive de styrènes et d' α -méthylstyrènes substitués sur le noyau. L'aptitude migratoire relative des groupes aryl, déterminée dans l'étude des produits d'oxydation de diphényl-1,1 éthylènes substitués sur le noyau, est en corrélation avec les constantes σ^+ de Brown, avec $\rho^+ = -2.27$.

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The oxidation of a great number of olefins by thallic salts has been the object of intensive recent studies (1-13), from the point of view of both preparative organic chemistry and of the interesting mechanistic implications. From Henry's fundamental studies, including product distributions and kinetic considerations, a basic mechanistic proposal has developed for the oxidation of a variety of simple olefins by Tl(III) in aqueous acid solutions (1, 2). The oxidation of cyclic olefins, e.g. the cyclohexenes, in aqueous (5) and in methanol (4) solutions, the oxidation of chalcones in methanol (8), as well as the oxidation of numerous aromatic olefins, e.g. styrene and derivatives thereof, by $Tl(NO_3)_3$ in methanol solution (6) have been investigated.

It appeared that the product distributions depend strongly on the specific experimental conditions. This prompted the present study on $Tl(NO_3)_3$ oxidation in methanol, which considers (*i*) kinetic aspects, (*ii*) the relative reactivity of substituted styrenes, and (*iii*) the migration of substituted phenyl groups in the oxidation of ring substituted 1,1-diphenylethylenes.

Results and Discussion

Kinetic Studies

The product analysis reported in detail in the Experimental Section indicates that the oxidation of styrene and selected derivatives thereof in methanol solution yields *quantitatively* the dimethylacetals of the corresponding arylethanals.²

$$ArCH = CH_2 + Tl(NO_3)_3 + 2 CH_3OH \rightarrow$$

 $ArCH_2$ — $CH(OCH_3)_2 + TINO_3 + 2HNO_3$

Styrene and α -methylstyrene were selected for the kinetic studies. At 25 °C, the reaction with thallic salt occurs rapidly, even at low concentrations of both reactants ($\sim 10^{-3} M$). The rate of olefin consumption follows second order kinetics [1],

$$[1] -d[Olefin]/dt = k[Olefin][Tl(III)]$$

as indicated by Fig. 1, expressed in terms of the integrated rate law.

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²The oxidation of styrene and *p*-bromostyrene by $Tl(NO_3)_3$ in methanol has been reported (6) to give appreciable amounts of glycol ethers, *i.e.* the 1-aryl-1,2-dimethoxyethanes (50–60%). Our investigation fails to confirm this, as explained in the Experimental section.

Olefin	 (°С)	[HNO ₃] (M)	[LiNO ₃] (M)	[H ₂ O] (M)	$(M^{-1} s^{-1})$
Styrene	5	3.5×10^{-3}	5×10^{-3}	0	3.2
	15			0	6.2
	25			0	12
	35			0	19
	25	5×10^{-3}	15×10^{-3}	0	13.5
	25	15×10^{-3}	5×10^{-3}	0	12.6
	25	20×10^{-3}	0	0	15.6
α-Methylstyrene	5	3.5×10^{-3}	5×10^{-3}	0	27
	15			0	48
	25			0	73
	35			0	110
Styrene	25	3.5×10^{-3}	5×10^{-3}	0	12
•				0.28	10.7
				0.56	8.5
				1.11	8.7

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TABLE 1. Rate constants for the Tl(NO₃)₃ oxidation of styrene and α -methylstyrene*

*[Tl(NO₃)₃] = $1.0 \times 10^{-3} M$, [olefin] = $1.0 \times 10^{-3} M$, solvent = methanol.



FIG. 1. Integrated second-order rate law for the TI(NO₃)₃ oxidation of styrene. (1) $T = 5 \,^{\circ}C$; (2) $T = 15 \,^{\circ}C$; (3) $T = 25 \,^{\circ}C$; (4) $T = 35 \,^{\circ}C$. Solvent = methanol; [TI(NO₃)₃] = $1.0 \times 10^{-3} M$; [styrene] = $1.0 \times 10^{-3} M$; [LiNO₃] = $5 \times 10^{-3} M$; [HNO₃] = $3.5 \times 10^{-3} M$.

The rate constants which were measured under various experimental conditions are indicated in Table 1.

The present kinetic results are thus in accord with those reported by Henry (1) for thallic oxidations in water and by Ouellette *et al.* (9) for the oxidation of styrenes by thallic acetate in acetic acid which both indicate the reactions to be first order in each reactant. It is noted, however, that our rate constants are about 50 times greater than those determined from the thallium acetate oxidation (9) in acetic acid. This can be due to the low stability of the Tl(III)-NO₃ complexes (14), resulting in a highly ionic character of the dominant species Tl^{3+} and $TlNO_3^{2+}$. Indeed, such complexes as TlX_2^+ and TlX_3 which should prevail in acetic acid for $Tl(OAc)_3$ are known to be less reactive (3, 10).

The results given in Table 1 also indicate that the rates are *not inhibited* by the presence of excess nitric acid. This supports the oxidation mechanism suggested by Henry (1) in which the slow step is the formation of the organo-thallic intermediate 1, eq. 2. In fact, if the decomposition [3] into final products were the slow process, the over-all rate would decrease as the nitric acid concentration is increased.

[2]
$$TIX_3 + ArCH = CH_2 + CH_3OH \xrightarrow{slow}$$

 $Ar - CH(OCH_3) - CH_2 - TIX_2 + HX$
[3] $1 + CH_3OH \xrightarrow{fast} Products + TIX + HX$

A consideration of all the results reported in the literature indicates that step [3] consists in a competition between two possible reaction paths. These are indicated in Scheme 1, which unifies the proposals which have been considered (2, 5, 6, 9) for various specific experimental conditions and is capable of explaining the depen-

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dence of the product distribution on the nature of the participating solvent.

As indicated in Scheme 1 for the phenylethylenes, two major modes (A and B) of reaction can take place, *i.e.*, (*i*) path A implying the participation and migration of the phenyl group, already demonstrated by labelling techniques (8, 9), and (*ii*) path B, implying the participation (or even migration) of the OR group of 1. Such a participation of OR should be favored over an S_N2 substitution of Tl by a solvent molecule, as demonstrated in the case of rigid cyclohexenes (5).

The discrimination between paths A and B depends on the solvent which is used and, hence, on the nature of the OR group in 1, and on the nature of the migrating group.³ The formation of dimethylacetals from the corresponding styrenes, which has turned out to be practically quantitative (see Experimental section), is a clear illustration of path A: the phenyl migration is at any rate considerably more important than any participation of the methoxy group. Such a behavior can be attributed to the fact that usually the methoxy group is a poor participating agent. The results which were observed for the 4'-methoxychalcone (8) also support the preferential migratory aptitude of the phenyl group over the participation of the methoxy group.

When the nature of the OR group is changed for a good participating group, it is conceivable that path B may be preferred. This would namely be the case in acetic acid solution (9), where OR =OAc, because the acetoxy is known to be an excellent participating group (11, 15). Alternatively, in cases where the phenyl group is replaced by a group whose migratory aptitude is poor, the relative importance of path B over A is increased to the extent that it may be significant even in methanol solution. This appears to occur in the oxidation of cyclohexene in methanol (6), where path B (formation of diether) represents 15%, as compared to 85\% for path A.⁴

It may now be regarded that the product formation (step [3]) is satisfactorily rationalized. From the kinetic point of view, it is, however, step [2] on which attention shall be focused.

The results in Table 1 indicate that α -methylstyrene reacts about 5–10 times faster than styrene, in the range of temperatures investigated. The effect of methyl substitution is thus similar but less pronounced to that observed for the relative reactivities of propylene vs. ethylene (2).

The activation parameters calculated from the results of Table 1 are $\Delta H^{\pm} = 9.9 \pm 0.5$ kcal, $\Delta S^{\pm} = -25 \pm 1.5$ e.u. (styrene) and $\Delta H^{\pm} = 7.1 \pm 0.5$ kcal, $\Delta S^{\pm} = -26 \pm 1.5$ e.u. (α -methylstyrene). These activation enthalpies are, hence, similar to the value (7.9 kcal) determined for the Tl(OAc)₃ oxidation of *p*-methylstyrene in acetic acid (9).

A more striking observation concerns the influence of water, even in small amounts, on the reaction rates: the presence of 1-2% of water causes a significant decrease of k (Table 1). This

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³No difference between thallium acetate and nitrate is observed in the product distribution under otherwise identical conditions.

 $^{{}^{4}}$ The values have been obtained by measuring the reaction products from the oxidation of cyclohexene, where they are, for path A, cyclopentanecarboxaldehyde and, for path B, the stereoisomeric 1,2-dimethoxycyclohexanes. These results are in full agreement with those reported in the literature (6).

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TABLE 2.	Influence of chloride ions on the rate
	of oxidation of styrene*

[C]-1	$R_{l} (M \text{ s}^{-1})$		
(M)	Observed	Calculated	
0	10.1×10^{-6}	10.1×10^{-6}	
2.5×10^{-4}	8.9×10^{-6}	8.0×10^{-6}	
5.0×10^{-4}	5.8×10^{-6}	5.9×10^{-6}	
7.5×10^{-4}	3.8×10^{-6}	4.0×10^{-6}	
1.0×10^{-3}	2.3×10^{-6}	1.8×10^{-6}	
1.5×10^{-3}	0.6×10^{-6}	0.9×10^{-6}	
2.0×10^{-3}	$\leq 0.3 \times 10^{-6}$	0	
5.0×10^{-3}	$< 3 \times 10^{-10}$	0	

*[Tl(ClO₄)₃] = $1.0 \times 10^{-3}M$, [styrene] = $1.0 \times 10^{-3}M$, T = 25 °C, [HClO₄] = 0.2 M, solvent = 80% (v/v) methanol - 20% (v/v) water.

can be explained either in terms of a preferential coordination of Tl(III) by water or else in terms of a partial hydrolysis of Tl(III), both of which processes would result in a less reactive thallium species.

The role of the coordination of the thallic ion is further illustrated by the influence of chloride ions, which are known to give stable complexes with Tl(III) (16), on the reaction rates. As indicated by the results in Table 2, chloride ions cause a marked retarding effect on the reaction rates. In order to avoid any interference by nitrate ions, these experiments were carried out in perchloric medium, using (for safety) a 80% (v/v) methanol - 20% water mixture as solvent.

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From these results, it may be concluded that $TlCl^{2+}$ is the only Cl-containing reactive species. This, because the rate drops considerably (to less than 3% of its initial value) when $[Cl^{-}]/[Tl(III)] = 2$, in which case the predominant species is $TlCl_{2}^{+}$, instead of $TlCl^{2+}$. Higher chloride concentrations prevent, for all practical purposes, the reaction to occur: this is observed with a ratio $[Cl^{-}]/[Tl(III)] = 5$, where the predominant species are $TlCl_{3}$ and $TlCl_{4}^{-}$.

These qualitative arguments, deduced from Table 2, lead to the following quantitative interpretation of these results. On the assumption that the stability constants of the various thallium complexes are in the present conditions at least as large as in water,⁵ the concentrations $[Tl^{3+}]$ and $[TlCl^{2+}]$ can be evaluated as in ref.

10. Hence, the overall initial rate R_i is

[4]
$$R_i = [\text{styrene}] (k_{TI}[TI^{3+}] + k_{TICI}[TICI^{2+}])$$

As indicated in Table 2, the calculated initial rates (eq. 4) are in satisfactory agreement with the corresponding experimental rates, thus supporting the interpretation given above.

The observation that the reactivity of TlCl^{2+} $(k_{\text{TlCl}} = 1.8 M^{-1} \text{ s}^{-1})$ is lower than that of Tl^{3+} $(k_{\text{Tl}} = 10.1 M^{-1} \text{ s}^{-1})$ indicates that the electrostatic effect due to the lowering of the ionic charge is the dominating factor. This is contrary to what had been observed previously in the case of the oxidation of 1,2-cyclohexane-dione under similar circumstances, where the present effect was overruled by an opposed "catalytic" effect (10).

Relative Reactivity of Substituted Styrenes

A further insight into the reaction mechanism is given by the study of substituent effects on the rate constants. The relative rates of oxidation of ring-substituted styrenes and α -methylstyrenes have been determined by a competitive method, using excess amounts of olefins with respect to Tl(III). Because the ratio of the products formed is equal to the ratio of the reaction rates, the ratio of the rate constants can be deduced from eq. 5, which is based on the assumption of first order reactions with respect to each olefin (eq. 1).⁶

[5] [Product-1]/[Product-2] =
$$k_1(\text{Ol-1}]/k_2[\text{Ol-2}]$$

It has been verified that k_1/k_2 is independent of the Tl(III) concentration and of the temperature (Table 3).

The reproducibility of the measurements is satisfactory (Table 4), despite the great differences of reactivity which are observed between the invidivual olefins. Each determination of k_1/k_2 has been repeated a minimum of 6 times, and the final results are indicated in Table 5 with a confidence limit of 95%.

It is noted that the results in Table 5 are expressed with respect to the unsubstituted phenylethylene in terms of k_X/k_H , where X stands for the substituent in the phenyl ring. These results

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⁵This assumption is verified by analogy with cases where the stability constants are known. There is an increase of stability for complexes of this type due to greater electrostatic interactions in the less polar solvent.

⁶This assumption is further confirmed by the fact that the ratios k_1/k_2 calculated by means of eq. 5 are independent of the ratios of the olefin concentrations.

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TABLE 3. Effect of the experimental conditions on the relative rates of Tl(III) oxidation of ring-substituted styrenes in methanol

Olefin-1 (M)	Olefin-2 (M)	T(°C)	[Tl(NO ₃) ₃]	k_1/k_2
<i>p</i> -Chlorostyrene, 1 <i>M</i>	Styrene, 1 M	-10	0.1	0.158
		0	0.1	0.161
		25	0.1	0.162
		25	0.02	0.155
<i>m</i> -Chlorostyrene, 1 M	Styrene, 0.1 M	25	0.02	0.027
0.5 M	0.1 M	25	0.02	0.030
p-Methylstyrene, 1 M	Styrene, 0.1 M	0	0.1	6.1
	,	25	0.1	5.9
<i>p</i> -Methoxystyrene, 1 M	p-Methylstyrene, 1 M	25	0.1	10.7*
	Styrene, 10M	25	0.1	60

*Corresponding to a value of 63 for k(p-methoxystyrene)/k(styrene).

TABLE 4. Competitive oxidation of *p*-methylstyrene (olefin 1) and styrene (2) in methanol at 25°

<i>p</i> -Methylstyrene	Styrene	
(<i>M</i>)	<i>(M)</i>	k_1/k_2
1.012	0.995	5.88
0.999	1.004	6.83
0.986	0.989	5.68
1.005	1.015	5.33
0.998	1.013	5.50
0.998	1.013	5.28
0.999	1.004	6.65

TABLE 5. Substituent effects on the rate of Tl(III) oxidation of ring-substituted styrenes and α -methylstyrenes in methanol at 25°

Parent olefins	Substituents (X)	$k_{\rm X}/k_{\rm H}$
Styrenes	m-Cl	0.028 ± 0.004 0.162 ± 0.015
	<i>р-</i> С/ Н	1,000
	p-CH ₃	5.9 ± 0.6
	p-CH ₃ O	63 ± 7
α-Methylstyrenes	p-Cl	0.150 ± 0.005
	Ĥ	1.000
	p-CH₃	6.4 ± 0.2

can be interpreted in terms of Hammett's relationship (Fig. 2).⁷

The negative slope $\rho = -4.2$ clearly indicates that the overall reaction is favored by electronreleasing substituents; the large ρ value reflects the extreme sensitivity of thallic oxidations to



FIG. 2. A verification of Hammett's relationship for the rates of Tl(III) oxidation of ring-substituted styrenes (1) and α -methylstyrenes (2) in methanol. The scale for (2) is shifted by 1 log unit ($\sigma(p$ -CH₃O) = -0.268; $\sigma(p$ -CH₃) = -0.170; $\sigma(H) = 0$; $\sigma(p$ -Cl) = +0.227; $\sigma(m$ -Cl) = +0.373).

electronic effects. Such a behavior has been noted previously for alkyl substituted ethylenes (2) and for styrenes in acetic acid solution (9). In the latter case, a similar dependence of the reaction rates on substituent effects has been noted, although in acetic acid the product distribution

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⁷This correlation is far superior to that which can be obtained using Brown's σ^+ values.

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is quite different from that observed in methanol. This is in line with the earlier suggestion that the formation of intermediate 1 is rate determining in both methanol and acetic acid.

The ring-substituted α -methylstyrenes react approximately 10 times faster than their styrene analogs. The only oxidation products are the corresponding phenylacetones (Table 1, Experimental section), and *no methylacetophenone could be detected*. This not only indicates that pathway A is followed, but also that any methyl migration is negligible. From the results in Table 5, it also follows that $\rho = -4.2$. Hence, from the observation that the same ρ values are observed for the styrenes and for the α -methylstyrenes, it can be deduced that the methyl group does not exhibit any steric effect which would perturb the transmission of the electronic effects due to the aromatic ring.

Relative Migratory Aptitude of Aryl Groups

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Ouellette's studies (9) on the oxidation of styrenes in acetic acid have provided interesting information on the migratory aptitudes of aryl groups. These results, which fit nicely into the proposed mechanism (Scheme 1), represent from this point of view a comparison between the migratory aptitude of the aryl group (path A) vs. the participation of OR (path B). The results indicate that electron-releasing substituents on the phenyl group favor its migration.

In methanol solution, however, only path A implying phenyl migration is followed. The relative migratory aptitude of aryl groups can be studied from the competition between two aryl groups under like environment. Derivatives of 1,1-diphenylethylene were chosen for this purpose. Thus, two different carbonyl compounds are formed, depending upon which aryl group has undergone migration (Scheme 2). The deoxybenzoine 2 arises from the migration of the unsubstituted phenyl group, whereas 3 is due to the migration of the substituted one.

TABLE 6. Relative migratory aptitude of aryl groups in the Tl(III) oxidation of 1,1-diphenylethylenes in methanol at 25°

Substituent	Propor- tion of 2	Propor- tion of 3	$k_{ m x}/k_{ m H}$
<i>m</i> -Cl	0.115	0.885	0.130 ± 0.008
p-Cl н	0.341	0.659	0.520 ± 0.005 1 000
<i>p</i> -CH₃ <i>p</i> -CH₃O	0.838 ≥0.98	0.162 ≤0.02	5.17±0.07 ≥50

The results reported in Table 6 indicate that electron-releasing substituents attached to a phenyl group favor its migration. In this, the present results agree with those reported by Ouellette *et al.* (9) for the oxidations in acetic acid.

The relative migratory aptitudes are expressed in terms of k_x/k_H , which can be correlated by means of a Hammett equation (Fig. 3). The best fit is obtained by using Brown's σ^+ parameters. The $\rho^+ = -2.27$ value thus calculated for the aryl migration following only path A compares favorably with the ρ^+ value (-1.7) which was determined (9) from the competition between aryl migration and 1,2-diacetate formation.

The present results are, hence, in line with the previous suggestions (6, 8, 9) that the aryl groups migrate toward a carbon atom possessing a more or less developed positive character. The present mechanistic suggestion (Scheme 1) would require a $C^{\delta+}$ character, and the C---Tl bond cleavage is assumed to be concerted with the aryl migration. This is supported by the recent stereochemical study of the oxidation of rigid cyclohexenes (5) which indicated that the decomposition of the organo-thallic intermediate is *not* initiated by the cleavage of the C--Tl bond. The partial positive charge on the C atom under consideration would, of course, result from the important electron-affinity of the Tl to which it is attached.

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FIG. 3. Hammett plot for the relative migratory aptitudes of aryl groups in the Tl(III) oxidation of ringmonosubstituted 1,1-diphenylethylenes in methanol $(\sigma^+(p-CH_3O) = -0.778; \sigma^+(p-CH_3) = -0.311; \sigma^+(H) = 0; \sigma^+(p-Cl) = +0.114; \sigma^+(m-Cl) = +0.399).$

Conclusions

The oxidation of phenylethylenes by $Tl(NO_3)_3$ in methanol proceeds rapidly and selectively to give the products resulting from the migration of aryl groups, *i.e.* (*i*) the 1,1-dimethoxy-2phenylethanes from the corresponding styrenes, (*ii*) the phenylacetones from the α -methylstyrenes and (*iii*) the two possible deoxybenzoines from the 1,1-diphenylethylenes.

Kinetic results indicate the reaction to be first order in each reactant. The rate determining step appears to be the formation of the organothallic intermediate. The retarding effect of water and Cl^- ions on the reaction rates illustrates the importance of the state of coordination of Tl(III).

Electron-releasing substituents enhance strongly the overall rate of oxidation of ring-substituted styrenes and α -methylstyrenes. The oxidation of ring-substituted 1,1-diphenylethylenes in methanol indicates that electron-releasing substituents strongly favor the migration of the corresponding aryl group, which is in line with the view that the aryl groups migrate toward a C⁵⁺ atom.

Experimental

The thallic nitrate was prepared by dissolving 15 g of thallic oxide in 20 ml concentrated nitric acid, at 60 °C. After cooling, the crystallized $TI(NO_3)_3 \cdot 3H_2O$ was filtrated and dried in vacuum. The thallic perchlorate solution was prepared by dissolving thallic oxide in aqueous HClO₄. The olefins were purchased or prepared and purified by standard methods. The methanol was dehydrated following a standard procedure (17).

The identification of the reaction products was, in general, made by g.l.c. retention times, comparison with authentic samples, and n.m.r. analysis. The g.l.c. analyses were carried out by means of an F and M 5750 gas chromatograph using two different 6 ft columns. For the analysis of the reaction products from the ring-substituted styrenes, 10% Carbowax 20M on Chromosorb PAW-DMCS and Polyphenyl 6 ring columns were used at 142°. The same columns were used at 125° for the oxidation products of the various α -methylstyrenes. For the 1,1-diphenylethylenes, Silicone Rubber UC-W98 (150°) and Polyphenyl 6 ring (195°) columns were used.

The nature of the products, and their yields, obtained from the oxidation of all the olefins investigated, are given in Table 7.

The observation that the oxidation of styrene yields only the dimethylacetal of phenylacetaldehyde, was verified by a comparison with a commercial (Aldrich) sample of acetal. It was also verified that, after acid hydrolysis, only phenylacetaldehyde is obtained. However, to insure a complete hydrolysis, the methanol had to be evaporated and the acetal treated during 1 h with 2 NH₂SO₄. Otherwise, the g.l.c. analysis indicates the presence of unreacted acetal. These results were confirmed by test experiments carried out with authentic samples of acetal. The absence of 1-phenyl-1,2-dimethoxyethane in the reaction products was confirmed by means of authentic samples of this product. The acetal and the diether can be separated in g.l.c. on Carbowax 20 M columns and also possess n.m.r. spectra which facilitate their analysis. In the acetal, in CCl₄ solution, the two methoxy groups give a single signal at 3.20 p.p.m. The CH₂ group is revealed by a doublet at 2.8 p.p.m., and the tertiary H by a triplet at 4.4 p.p.m. In the diether, the methoxy groups give two signals at 3.20 and 3.25 p.p.m., the tertiary proton consists of a quartet centered at 4.2 p.p.m., and the CH₂ group a complex signal at 3.4 p.p.m.

The acetals obtained from the oxidation of substituted styrenes have been isolated, after filtration of the thallous nitrate, by washing the methanol solution with a carbonate solution, followed by an extraction by means of ether. The n.m.r. results in CCl₄ solution, with reference to TMS, are indicated in Table 8.

In all cases, the hydrolysis of the acetals has been made in order to confirm the production of the corresponding aldehyde.

The oxidation product from α -methylstyrene has been identified by a comparison with a sample of pure phenylacetone, by g.l.c. (on 2 different columns) and by n.m.r. analysis. The g.l.c. analysis, using acetophenone as internal standard, indicated a yield of 99% of phenylacetone. The n.m.r. spectra of the phenylacetones obtained from their corresponding α -methylstyrenes are indicated in Table 9.

The oxidation product from 1,1-diphenylethylene was identified in g.l.c. by a comparison with a sample of

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TABLE 7. Mass balance for the Tl(III) oxidation of selected phenylethylenes in methanol

Olefin	Olefin used (mmol)	Acetal (mmol)	Carbonyl compound (mmol)
Styrene	0.548	0.546*	
	20.0		16.4†
<i>p</i> -Methylstyrene	7.83	7.16‡	
<i>p</i> -Methoxystyrene	7.23	6.79‡	
<i>p</i> -Chlorostyrene	6.86	6.38‡	
α-Methylstyrene	0.740		0.735*
p-Methyl- α -methylstyrene	7.86		7.30‡
p-Chloro-α-methylstyrene	8.04		7.641
1,1-Diphenylethylene	0.536		0.520*
1-p-Anisyl-1-phenylethylene	7.20		6.78±§
1-p-Tolyl-1-phenylethylene	7.63		7.02‡§
1-p-Chlorophenyl-1-phenylethylene	7.90		7.50‡§
1-m-Chlorophenyl-1-phenylethylene	7.82		7.12‡§

*Obtained by g.l.c. of the reaction mixture after completion of the oxidation. †After hydrolysis of the acetal product. From 20.3 mmol of pure acetal, 17.5 mmol of phenylethanal was obtained. ‡After extraction and isolation of the reaction products. §Total amount of carbonyl compound, consisting of a mixture of the two isomeric deoxy-benzoines.

TABLE 8. N.m.r. spectra of the 1,1-dimethoxy-2-arylethanes produced in the Tl(III) oxidation of ring-substituted styrenes in methanol

Substituent X	δ _{aryl} (p.p.m.)	δ _{CH2} (d) (p.p.m.)	δ _{сн} (t) (p.p.m.)	δ _{осн3} (s)* (p.p.m.)
m-Cl	7.18	2.80	4.40	3.25
p-Cl	7.15	2.80	4.40	3.25
Ĥ	7.10	2.80	4.40	3.20
$p-CH_3$	6.90	2.75	4.40	3.20
p-CH ₃ O	6.50	2.60	4.35	3.05

*Acetal-methoxy group. For the *p*-methoxy and the *p*-methyl ring substituents, the corresponding protons appear at 3.50 p.p.m. (s) and at 2.25 p.p.m. (s).

TABLE 9. N.m.r. spectra of arylacetones produced in the TI(III) oxidation of ring-substituted α -methylstyrenes in methanol

Substituent X	δ _{aryi} (p.p.m.)	δ _{сн2} (s) (p.p.m.)	δ _{сн3} (s)* (p.p.m.)
p-Cl	6.80	3.40	1.95
ਸ	6.80	3.35	1.90
p-CH₃	6.60	3.30	1.85

*Acetone methyl group. The *p*-methyl ring-substituent appears at 2.15 p.p.m. (s).

deoxybenzoine is observed in g.l.c., using p-methoxybenzophenone as internal standard. The identification of all the reaction products was made by comparison with pure samples of 4'-methoxy-, 4'-methyl-, and 4'-chloro-deoxybenzoines, and 4-methoxy-, 4-methyl-, and 4-chloro-deoxybenzoines, all of which were prepared and purified according to literature methods (18).

Kinetic Method

The course of each reaction was followed by ultraviolet spectrophotometry at 270-290 mµ, thus measuring the decrease in olefin concentration. The interpretation of the results was made by means of the integrated second order rate law $x/(a - x) = (A_0 - A_t)/A_t - A_\infty) = kat$, where a = [olefin] = [Tl(III)] and x = concentration ofreaction product at time t. The quantities A_0 , A_t , and A_{∞} are, respectively, the absorbances at time t = 0, t = t, and $t = \infty$. The rate constant k was calculated from the regression line, as illustrated in Fig. 1. It has been verified that no variation in k occurs when the concentration of the reactants was changed by a factor of 4. Reproducible k values can only be obtained when due care is taken to avoid any polymerization of the olefin while setting up the experiments. The statistical analysis of the results indicates a reproducibility of the k values within 5%.

The competitive kinetic measurements were made by adding 5 ml of a 0.1 M solution of thallic nitrate to 5 ml of a solution 1 M in each olefin. In most cases, styrene was used as reference compound. Because of the great difference in reactivity between styrene and m-chlorostyrene, 0.1 M styrene solutions and concentrations of 0.5-1.0 M of m-chlorostyrene were used, with a 0.02 M concentration in thallic nitrate. For the experiments with p-methoxystyrene, p-methylstyrene was used as reference.

The possible influence of nitrate ions was examined. The kinetic study has revealed a slight increase of the reaction rate by added nitrate ions. However, in the present experimental conditions, a 3-fold excess of nitrate ions in form of LiNO3 does not alter significantly the ratios $k_{\rm X}/k_{\rm H}$. For example, in the presence of excess NO₃⁻, $k_{\rm X}/k_{\rm H} = 6.7$ for the *p*-methylstyrene/styrene system, which compares favorably with the results reported in Table 3.

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