EFFECTS OF SALTS ON THE KINETICS OF OXIDATION OF ALKENES BY THALLIC SALTS IN AQUEOUS SOLUTIONS*

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The kinetics of oxidation of alkenes by thallic sulphate in aqueous solutions, involving the two reaction steps — the hydroxythallation and the dethallation — was studied, and the effect of salts on the kinetics was examined; this made it possible to specify more precisely the reaction mechanism and to suggest a qualitative model of the reaction coordinate. It was found that in homogeneous as well as in heterogeneous reaction conditions, the reaction can be accelerated appreciably by adding tetraalkylammonium salts. These salts not only operate as catalysts of the phase transfer, but also exert a significant kinetic effect, which can be explained with a simplification in terms of a stabilization of the transition state of the reaction.

Oxidation of alkenes by thallic ions in aqueous solutions results in the formation of two characteristic products: one of them is always a vicinal diol in which the carbon skeleton of the starting alkene is preserved, the other product is a carbonyl compound (aldehyde or ketone) whose nature depends on the structure of the alkene[1]. Oxidation of terminal n-alkenes leads to a single ketone, oxidation of internal alkenes to isomeric ketones. A significant feature of oxidation of C_2 substituted terminal alkenes is the fact that in addition to the aforesaid substances, an aldehyde forms to an appreciable extent.

The reaction mechanism comprises three states[1]: formation of the π-complex by the electrophilic attack of the Tl^{3+} ion on the double bond of the alkene; conversion of the π-complex to the σ-complex — this is the reaction rate-determining step; and decomposition of the hydroxythallic adduct by the nucleophilic attack of the solvent, controlling the diol-to-carbonyl ratio.

As found by Henry[2], the oxythallation rate depends on the concentration of neutral salts in the system, this effect being associated with the activity of water. Study of the kinetics of decomposition of the oxythallic adduct C_6H_5—CH(OCH_3)—$CH_2Tl(OAc)_2$ led to the interesting and surprising finding that if higher initial concentrations of the reacting components are applied (above 0·1 mol l⁻¹), the situation is opposite to that encountered with lower concentrations — it is the decomposition of the oxythallic adduct that represents the rate-determining step in the oxidation[3]. In the case of oxidation of alkenes by thallic sulphate in free sulphuric acid there is a transition from the kinetic to the diffusion region at these concentrations[4]. Under these conditions the reaction is practically pseudo-zero-order, as the dependence of the conversion of Tl^{3+} to Tl^+ on time is linear.

The salt effects on the oxidation of alkenes by thallic salts have only been studied from the point of view of their influence on the reactivity of the starting materials and only for the oxidation rate-determining step, which in the case of the homogeneous phase kinetics is the oxythallation. The effect of additions of salts on the dethallation reaction has not been studied at all. We considered it reasonable to examine the effects of salts on the dethallation reaction and also on the overall course of the oxidation from the point of view of their influence on the stability of the transition state. Oxidation by thallic sulphate of allyl alcohol served as a homogeneous phase model reaction and oxidation of 2,4,4-trimethyl-1-pentene as a heterogeneous phase model reaction.

EXPERIMENTAL

Chemicals. The thallic sulphate oxidant solution was prepared by electrolytic oxidation of an aqueous solution of thallous sulphate (pure, Lachema, Brno) in the presence of sulphuric acid[5]. The concentration of thallium was determined by two independent methods, *viz.* titration of the Tl^+ ions with a KIO_3 titrant solution[6] and titration of iodine, liberated by the reaction of Tl^{3+} with KI, with an $Na_2S_2O_3$ standard solution[7]. 2,4,4-Trimethyl-1-pentene was prepared in chromatographic purity of 99·5% by rectification of trimethylpentene[5]. The other chemicals were commercial products of Lachema, Brno, reagent grade purity.

Kinetic methods. The oxidation of alkenes by thallic sulphate could be conducted at room temperature, at which it proceeds sufficiently rapidly. The kinetics of oxidation in the homogeneous phase was monitored UV spectrophotometrically at 200—240 nm at room temperature using a Unicam SP 700 instrument. The effect of salts on the kinetics of both the hydroxythallation and the dethallation was monitored UV spectrophotometrically at 205 nm on a Unicam SP 500 apparatus using cells thermostatted to $25 \pm 0.1°C$. Allyl alcohol was chosen as the substrate with regard to its perfect solubility in water, ensuring homogeneity of the solution. Oxidation in solutions containing $1.74 . 10^{-3}$ mol l^{-1} allyl alcohol, $1.26 . 10^{-4}$ mol^{-1} $Tl_2(SO_4)_3$ and 0.05 mol l^{-1} H_2SO_4 served as the standard reaction. The oxidation in heterogeneous phase was conducted in a 250 ml three-necked reactor fitted with a KPG stirrer and a thermometer. The whole reactor was submerged in a water thermostat maintaining a constant reaction temperature of $25 \pm 0.1°C$. The oxidant solution was represented by aqueous solution of $Tl_2(SO_4)_3$ with the Tl^{3+} ion concentration 0.251 mol l^{-1}, containing 0.455 mol l^{-1} H_2SO_4 requisite for preventing hydrolysis of the salt. The reaction mixture involved 150 ml of the oxidant solution and 20 ml of trimethylpentene. The stirrer rotated with the frequency of 1 200 r.p.m. Samples were taken during the reaction and the concentration of Tl^{3+} was determined in them by iodometric titration; from the concentration values, the degree of conversion (X) of Tl^{3+} to Tl^+ was calculated.

RESULTS AND DISCUSSION

The effect of salts on the oxidation was examined by studying the kinetics in both the homogeneous and the heterogeneous phases. For a verification of the method, the oxidation was monitored spectrophotometrically in the UV region. The spectral

changes in the 200—240 nm region are depicted in Fig. 1. The highest changes are seen in the 205 nm range. Virtually instantly after the mixing of allyl alcohol with the oxidant, the absorbance increases over the entire region investigated (hydroxythallation), with a subsequent slow decrease of absorbance in the region of 200 to 215 nm (dethallation). The final spectrum (*3*) corresponds to the overall stoichiometric course of the reaction

$$Tl^{3+} + CH_2{=}CH{-}CH_2OH + H_2O \rightleftarrows Tl^+ + CH_3COCH_2OH + 2H^+ \quad (A)$$
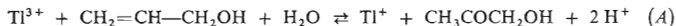
There appears no isosbestic point in the spectra, which warrants the assumption that the intermediate hydroxythallic adduct is formed in an appreciable concentration. A typical course of oxidation of allyl alcohol, as observed at 205 nm, is shown in Fig. 2. Obviously, the course of the reaction divides into two parts. As follows from our previous works[8], oxidation of alkenes by thallic salts is a second-order reaction. Since the kinetics measurements were conducted using a sufficient excess of allyl alcohol, the kinetic of the hydroxythallation will have the character of a pseu-
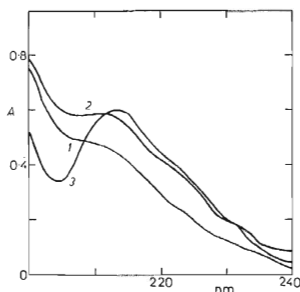

FIG. 1

Spectral Changes During Reaction of Tl^{3+} ($1 \cdot 1 \cdot 10^{-4}$ mol l^{-1}) with Excess Allyl Alcohol ($2 \cdot 86 \cdot 10^{-3}$ mol l^{-1})

1 Initial spectrum (sum of the spectra of the components); *2* approx. 1 min after mixing; *3* final spectrum (after 3 h). Measured in 2 cm cells.
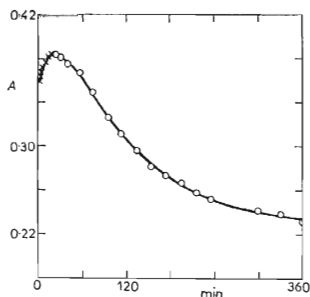
FIG. 2

Spectral Monitoring of the Oxidation of Allyl Alcohol at 25°C

Conditions given in the Experimental; measured in 1 cm cells. × Hydroxythallation, ○ dethallation.

TABLE I

Effect of Salts on the Rate Constant of Hydroxythallation[a] k_1 (l mol^{-1} s^{-1})

Salt concentration mol l^{-1}	NaClO$_4$	LiNO$_3$	NH$_4$NO$_3$	(n-C$_4$H$_9$)$_4$NCl	(C$_2$H$_5$)$_4$NI
0·0125	—	—	—	0·79	—
0·025	—	—	—	3·37	1·54
0·05	—	—	1·00	40·11	6·59
0·1	2·10	—	2·33	[b]	13·28
0·2	11·70	0·89[c]	14·16	[b]	21·88[d]
0·3	19·45	—	22·75	[b]	[b]
0·4	—	3·19	33·90	[b]	[b]
0·5	—	7·20	[b]	[b]	[b]
0·6	—	29·57	[b]	[b]	[b]

[a] Values for $c = 0$ mol l^{-1} ($k_1^0 = 0.25$ l mol^{-1} s^{-1}) taken from ref.[8]; [b] too fast for conventional measurements; [c] for $c = 0.25$ mol l^{-1}; [d] for $c = 0.15$ mol l^{-1}.
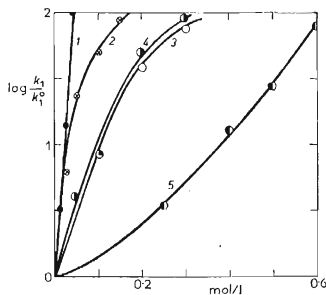

Fig. 3

Dependence of the Rate of Allyl Alcohol Hydroxythallation on the Concentration of Salts at 25°C

k_1 2nd order rate constant after the addition of salt, k_1^0 2nd order rate constant of the standard reaction (without addition of a salt). 1 (n-C$_4$H$_9$)$_4$NCl, 2 (C$_2$H$_5$)$_4$NI, 3 NaClO$_4$, 4 NH$_4$NO$_3$, 5 LiNO$_3$.
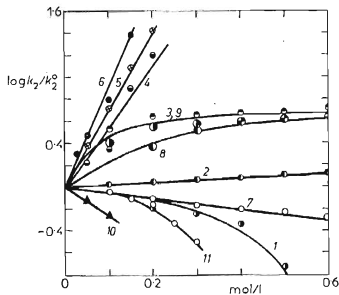
Fig. 4

Dependence of the Rate of Dethallation on the Concentration of Salts at 25°C

k_2 1st order rate constant after the addition of salt, k_2^0 1st order rate constant of the standard reaction. 1 Li$_2$SO$_4$, 2 (NH$_4$)$_2$.SO$_4$, 3 NH$_4$Cl, 4 (CH$_3$)$_4$NCl, 5 (C$_2$H$_5$)$_4$NI 6 (n-C$_4$H$_9$)$_4$NCl, 7 NaClO$_4$, 8 LiNO$_3$, 9 NH$_4$NO$_3$, 10 NaCl, 11 K$_2$SO$_4$.

do-first-order reaction,

$$-d \ln [Tl^{3+}]/dt = k_{obs}[Tl^{3+}] = k_1[\text{allyl alcohol}][Tl^{3+}],\qquad(1)$$

hence

$$k_1 = k_{obs}/[\text{allyl alcohol}].\qquad(2)$$

The Guggenheims method[9] was applied to the determination of k_{obs} from the spectra. For a pseudo-first-order reaction,

$$\log(A_t - A_\infty)/\Delta t = -k_{obs}/2{\cdot}303,\qquad(3)$$

hence

$$k_{obs} = -2{\cdot}303 \log(A_t - A_\infty)/\Delta t,\qquad(4)$$

where A_t and A_∞ are the absorbance in the time t and after the finishing of the reaction, respectively.

Effect of Salts on the Homogeneous Phase Kinetics

For a rough estimation of the effect of the electrolyte concentration on the rate constant, the approximate concept can be used that an addition of the electrolyte to the reaction mixture results in an increase in the polarity of the medium, so that the change effected is in the same direction as that brought about by increasing the polarity of the solvent[10].

The effect of salts on the rate of hydroxythallation of allyl alcohol is shown in Fig. 3 and Table I. The hydroxythallation rate increases with growing concentration of the salt, the effect increasing in the order $LiNO_3 < NaClO_4 \approx NH_4NO_3 < < (C_2H_5)_4NI < (n\text{-}C_4H_9)_4NCl$. In the case of $NaClO_4$ and $LiNO_4$, this effect is in accordance with the observations of Henry[2]. The perchlorate and the nitrate anions possess only a weak ability to form complexes with Tl^{3+}, the decisive factor is thus the solvation of the activated complex; therefore, the hydroxythallation rate rises with the concentration of the salts. In the case of $(C_2H_5)_4NI$ and $(n\text{-}C_4H_9)_4NCl$, the reaction is even more spurred than in the case of $LiNO_3$ and $NaClO_4$. This may be explained in terms of a stabilization of the transition state, TS2, by the $R_4N^\oplus$ cation, which must be appreciable enough to prevail over the effect of the Cl^- or I^- anions, known[2] to form nonreactive complexes with Tl^{3+} ions and thus to bring about deactivation of the latter.

The effect of the concentration of the salts on the rate of the dethallation reaction is shown in Fig. 4 and Table II. Except for $LiNO_3$, inorganic salts bring about a decrease in the dethallation rate. This effect increases in the order $NaClO_4 < < Li_2SO_4 \approx K_2SO_4 < NaCl$. The slowing-down is probably due to the formation of ion pairs of the type $[CH_2(OH)CH(OH)Tl^{2+}]Y_n$ ($n = 2$ for $Y = Cl^-$, ClO_4^-,

and $n = 1$ for $Y = SO_4^{2-}$) effecting stabilization of the initial hydroxythallic adduct by preventing access of molecules of the solvating agent (water molecules in our case), which results in a retardation of the hydrolysis. The general ionic effect may play a part, too, shifting the equilibrium in favour of the reagents. It is interesting that the dethallation is slowed down by addition of $NaClO_4$. Regarding the ability of the ClO_4^- anion to form complex compounds, comparable with that of the NO_3^- anion, one could expect a reverse effect, *i.e.* acceleration of the reaction. The situation with $NaClO_4$ is apparently more complicated, and a complex influence can be expected in both the initial and the transition states.

Addition of tetraalkylammonium salts $\left(R_4N^{\oplus}, \text{ with } R = H, CH_3, C_2H_5, n\text{-}C_4H_9\right)$ brings about a rise in the hydrolytic decomposition rate. Similarly as in the case of the hydroxythallation, the effect of the $R_4N^{\oplus}$ cation obviously prevails over that of the Cl^-, I^-, or SO_4^{2-} anions. The transition state, TS3, is stabilized by facilitating the proton transfer from the substrate to water with simultaneous increase in the acceptor abilities of the salts and by weakening the C–Tl bond, which results in a lowering of the ΔG^+ value and thus in an acceleration of the dethallation.

Based on the kinetic measurements, a simplified model of the effect of salts on the course of the oxidation reaction can be suggested, as shown in Fig. 5.
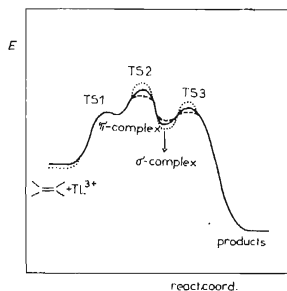

Fig. 5

Effect of Salts on the Course of the Oxidation

——— Standard reaction, — — — — acceleration of the reaction, · · · · · · · slowing down of the reaction.
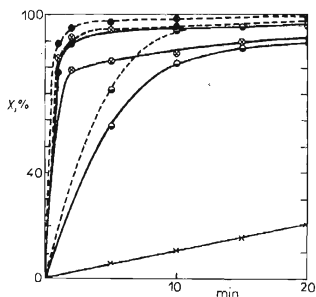

Fig. 6

Dependence of the Conversion of Tl^{3+} to Tl^+ During Oxidation of 2,4,4-Trimethyl-1-pentene on the Concentration of Salts at 25°C

× Standard reaction, ⊖ $(CH_3)_4NCl$, ⊗ $(C_2H_5)_4NI$, ● $n\text{-}C_4H_9)_4NCl$; ——— $0·1 \text{ mol } l^{-1}$, — — — $0·2 \text{ mol } l^{-1}$.

TABLE II
Effect of Salts on the Rate Constant of Dethallation^a k_2 (10^3 s^{-1})

Salt concentration mol l^{-1}	K$_2$SO$_4$	Li$_2$SO$_4$	(NH$_4$)$_2$SO$_4$	NH$_4$Cl	(CH$_3$)$_4$NCl	(C$_2$H$_5$)$_4$NI	(n-C$_4$H$_9$)$_4$NCl	NaClO$_4$	LiNO$_3$	NH$_4$NO$_3$	NaCl
0·05	4·70	—	—	—	10·60	11·51	14·99	—	—	—	3·86
0·1	4·45	4·51	5·29	17·34	11·14	31·74	32·12	—	11·36	12·61	2·88
0·15	3·97	—	—	—	38·64	62·61	122·11	—	—	—	b
0·2	3·48	3·32	5·56	21·82	80·68	136·97	10·15^c	3·66	11·82	18·63	b
0·25	3·88	—	—	—	d	d	d	—	—	—	b
0·3	1·61	2·92	5·85	22·25	d	d	d	3·47	16·84	19·33	b
0·4	b	2·43	6·20	23·35	d	d	d	3·26	20·51	21·19	b
0·5	b	0·98	6·57	23·75	d	d	d	3·18	34·84	21·86	b
0·6	b	—	6·73	27·33	d	d	d	2·75	38·21	22·67	b

^{a} Value for c = 0 mol l^{-1} (k_2^0 = 5·09 . 10^{-3} s^{-1}); ^{b} too slow; ^{c} value for c = 0·025 mol l^{-1}; ^{d} too fast for conventional measurements.

Effect of Salts on the Heterogeneous Phase Kinetics

In order to test whether the effect of R_4N^+ salts on the rate of oxidation of alkenes by thallic salts in conditions of macrokinetics is the same as in the homogeneous phase, the kinetics of oxidation of trimethylpentene was investigated in the heterogeneous phase, in conditions that may occur in technical practice. The effect of concentration of tetraalkylammonium salts on the course of conversion of Tl^{3+} to Tl^+ effected by excess 2,4,4-trimethyl-1-pentene is depicted in Fig. 6. The dependence of the conversion on time is linear up to approximately 80%. Assuming that the reaction proceeds only in the Tl^{3+} solution phase, in which the reacting olefin is very low soluble, we can expect the kinetics to be pseudo-zero-order nature. The observations made suggest the concept of a reaction comprising at least two steps, the first of them, the formation of the hydroxythallic complex, being here considerably faster than its decomposition, so that the concentration of its intermediate product is steady over a wide region of concentrations of the starting substances. For this reason the reaction is slowed down only in the stage of a higher degree of conversion. The linear part can be thus supposed to represent the diffusion region of the process in question. As can be seen from Fig. 6, addition of tetraalkylammonium salts effects a 20-fold to 60-fold acceleration of the reaction, the effect increasing in the order $NH_4Cl < (CH_3)_4NCl < (C_2H_5)_4NI \approx (n\text{-}C_4H_9)_4NCl$, the same as in the case of the homogeneous phase kinetics. It is apparent from Fig. 6 that the oxidation of 2,4,4-trimethyl-1-pentene by thallic sulphate proceeds completely in the diffusion region. The effect of the $R_4N^\oplus$ cations on the oxidation can be thus expected to be not only purely kinetic (as is the case in homogeneous phase), but also to cause an enhanced transfer of the alkene from the organic phase into the aqueous phase, in which the chemical reaction occurs, owing to the easier transition of the substances on the interface (phase catalysis effect). This is corroborated by the fact that the reaction is accelerated most by $(n\text{-}C_4H_9)_4NCl$, which is an efficient phase transfer catalyst[11]. Micellar catalysis can be ruled out in this case, since the tetra-n-butylammonium cation does not form micelles.

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