

# Solvolysis of the complexes of trivalent thallium with olefins\*

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*Dedicated to Professor Dr. Ing. M. Hrušovský, DrSc., in honour  
of his 65th birthday*

The influence of ionization power of solvent (water—ethanol mixture) on solvolysis of the  $\sigma$  complexes of trivalent thallium with olefins was investigated. It has been ascertained that the rate of solvolysis decreases with increasing concentration of ethanol. The two-parameter Grunwald—Winstein equation was applied to the study of reaction mechanism. The low values of the parameter  $m$  in the solvolysis of allyl alcohol and 2,4,4-trimethyl-1-pentene suggest the  $S_N2$  mechanism for  $RCH=CH_2$  and  $R^1R^2C=CH_2$  alkenes. On the other hand, the relatively high value of  $m$  in the solvolysis of 2,4,4-trimethyl-2-pentene allows to assume the  $S_N1$  mechanism for the solvolysis of internal branched alkenes.

Было исследовано влияние ионной силы растворителя вода—этанол на сольволиз  $\sigma$ -комплексов таллия(III) с олефинами. Было найдено, что при повышении концентрации этанола скорость сольволиза понижается. Для определения механизма реакции было использовано уравнение Грунвальда—Винштейна с двумя параметрами. Низкие значения параметра  $m$  при сольволизе аллилового спирта и 2,4,4-триметил-1-пентена свидетельствуют в пользу  $S_N2$  механизма сольволиза алкенов типа  $RCH=CH_2$  и  $R^1R^2C=CH_2$ . Относительно высокое значение  $m$  при сольволизе 2,4,4-триметил-2-пентена позволяет предполагать  $S_N1$  механизм сольволиза разветвленных алкенов.

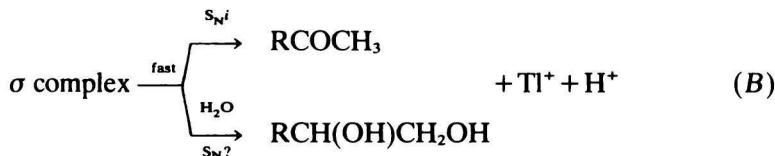
Recently, considerable attention was paid to the oxidation of alkenes by thallic salts [1—3]. The oxidation in aqueous medium gives two products. The first one is

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For Part VII see Strašák, M. and Majer, J., *J. Org. Chem.* 45, 3580 (1980).

a vicinal diol in which the structure of the original carbon skeleton is preserved and the second one is a carbonyl compound (aldehyde and/or ketone). The formation of these products as well as the reaction kinetics can be demonstrated by the following equations



The rate-determining step of the whole reaction is the formation of the  $\sigma$  complex [4–6]. The rightness of this assumption is confirmed by the fact that the oxythallic adduct could be isolated under certain conditions (water-free medium) [7–9]. Moreover, a spectral evidence of the formation of the  $\sigma$  complex in the oxidation of alkenes in aqueous medium was also given [10, 11]. The decomposition of the  $\sigma$  complex (B) is the product-determining step of reaction [6].

While a great number of papers [4–6, 10, 12–17] are concerned with kinetics and reaction mechanism of the formation of the  $\sigma$  complex (oxythallation), its decomposition has been given much less attention. On the basis of mechanistic studies, *Henry* has postulated [6] that for  $\text{C}_2$ – $\text{C}_4$  alkenes the solvolysis obeys the  $\text{S}_{\text{N}}1$  mechanism like the hydration of alkenes. Conversely, on the basis of investigations concerning the influence of the structure of alkenes [14] and reaction medium [18] on selectivity of the oxidation, the author of this paper has assumed [3] that for  $\text{RCH}=\text{CH}_2$  alkenes the solvolysis follows the  $\text{S}_{\text{N}}2$  mechanism while a borderline case between the  $\text{S}_{\text{N}}1$  mechanism and the  $\text{S}_{\text{N}}2$  mechanism may appear with  $\text{R}^1\text{R}^2\text{C}=\text{CH}_2$  and internal alkenes. All these conclusions are, however, drawn on the basis of indirect evidence. Thus the aim of this study was to submit an experimental distinction between the monomolecular and bimolecular solvolytic decomposition of oxythallic adduct ( $\sigma$  complex).

## Experimental

### Chemicals

The oxidation solution of thallium(III) sulfate was prepared by electrochemical oxidation of thallium(I) sulfate according to the procedure described in [19]. The concentration of the  $\text{Tl}^{3+}$  ions was determined by titrating the iodine liberated in the reaction between  $\text{Tl}^{3+}$  and KI with a standard solution of  $\text{Na}_2\text{S}_2\text{O}_3$  [20].

Allyl alcohol (pure, Lachema, Brno) was redistilled before use. 2,4,4-Trimethyl-1-pentene (244TMP1) and 2,4,4-trimethyl-2-pentene (244TMP2) of 99.5% chromatographic purity were obtained by distillation of an oligomeric mixture of isobutylene (ChZJD, Bratislava) according to the procedure described in [19].

Redistilled water was used for the preparation of all solutions. Other chemicals used were anal. grade reagents (Lachema, Brno). Ethanol was of spectral purity (Spolana, Neratovice).

### Kinetics

The kinetics of solvolysis of the  $\sigma$  complexes of  $Tl^{3+}$  with the above alkenes was investigated by ultraviolet spectrophotometry [11] at 205 nm by measuring the decrease in absorbance due to formation of the  $Tl^+$  cation (*B*). The spectral investigation was carried out with a spectrophotometer Unicam SP 500 in temperature-controlled 1 cm cells at  $25 \pm 0.1^\circ C$ . The experimental conditions were as follows:  $[Tl_2(SO_4)_3] = 2.51 \times 10^{-4} M$ ,  $[H_2SO_4] = 0.1 M$ ,  $[allyl\ alcohol] = 7.36 \times 10^{-3} M$ ,  $[244TMP1] = [244TMP2] = 6.41 \times 10^{-3} M$ .

The kinetic measurements were evaluated graphically by the method of least squares with a calculator Hewlett—Packard HP-97. The program 1 KIN 1 elaborated for calculation of the rate constant of the first-order reactions [21] was used.

### Results and discussion

The influence of solvent on solvolysis of the  $\sigma$  complex of  $Tl^{3+}$  with the investigated olefins is shown in Table 1. It is evident that a significant decrease in the rate of solvolysis appears with decreasing polarity and ionization power of the solvent. For allyl alcohol, the reaction rate decreases to one seventh and for 244TMP1, to one thirtieth. This decrease is especially conspicuous in case of 244TMP2 (to one hundred thirtieth approximately). This qualitative estimation is sufficient to make clear that the transition state of solvolysis of the  $\sigma$  complex of  $Tl^{3+}$  with internal alkenes is much more sensitive to the ionization power of solvent than it is in case of solvolysis of the  $\sigma$  complex of  $Tl^{3+}$  with  $RCH=CH_2$  and  $R^1R^2C=CH_2$  alkenes. The increase in the rate of solvolysis of the  $\sigma$  complexes of  $Tl^{3+}$  with ionization power of solvent is in accordance with the suggested mechanism [4—6] which involves heterolytic cleavage of the C—Tl bond. An increase in the ionization power of solvent brings about a decrease in stability of the  $\sigma$  complex (it is relatively stable in water-free medium) and simultaneously stabilizes the transition state of solvolytic reaction.

One of the factors which most affect the reaction rate is the medium in which the reaction takes place. The solvent molecules are effective in chemical reaction as a ionization medium electrophile—nucleophile. It is obvious from the reaction mechanism of decomposition of the  $\sigma$  complex (*B*) that this effect sets in owing to solvolysis. As solvolytic reactions involve nucleophile push and electrophile pull,

Table 1

Influence of ionization power of the solvent on the rate of solvolysis of the  $\sigma$  complexes of  $Tl^{3+}$  with olefins at 25°C

v/v % C <sub>2</sub> H <sub>5</sub> OH	Y <sup>a</sup>	$k \cdot 10^4/s^{-1}$ (graph/calc)		
		Allyl alcohol	244TMP1	244TMP2
0	3.493	7.98/6.47 ± 0.39	6.52/10.21 ± 1.49	64.88/63.98 ± 4.39
10	3.10	5.45/5.17 ± 0.12	4.30/ 6.31 ± 0.84	45.99/49.18 ± 5.08
20	2.82	5.04/4.99 ± 0.18	3.99/ 3.97 ± 0.24	24.87/25.56 ± 1.86
30	2.45	4.30/4.41 ± 0.20	3.22/ 3.49 ± 0.09	18.54/18.25 ± 0.97
40	2.08	3.99/3.62 ± 0.08	2.54/ 2.86 ± 0.07	8.91/ 8.20 ± 0.62
50	1.60	3.53/3.27 ± 0.21	2.16/ 2.20 ± 0.05	7.14/ 5.67 ± 0.42
60	1.20	3.06/2.98 ± 0.14	1.64/ 1.61 ± 0.08	3.47/ 2.94 ± 0.31
70	0.57	2.56/2.44 ± 0.17	1.11/ 1.10 ± 0.06	1.66/ 1.26 ± 0.14
80	0	2.19/2.07 ± 0.11	0.80/ 0.79 ± 0.03	0.83/ 0.61 ± 0.06
90	-0.82	1.71/1.62 ± 0.08	0.52/ 0.48 ± 0.03	0.25/ 0.17 ± 0.02
100	-2.03	1.20/1.17 ± 0.06	0.26/ 0.22 ± 0.02	0.056/0.043 ± 0.004

a) Values taken from paper [25].

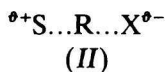
we may use a macroscopic empirical parameter of solvent for the determination of reaction mechanism. By comparing the sensitivity of reactions with respect to polarity of the solvent or its ionization power and nucleophilicity, we may obtain mechanistic information which is to be used as an evidence of a certain reaction mechanism. The basic idea is the qualitative rule of *Hughes* and *Ingold* [22] according to which an increase in solvent polarity brings about an increase in reaction rate for those reactions in which a greater separation of charge in transition state takes place. This assumption has been put in quantitative form by *Grunwald* and *Winstein* [23] who propose for correlation the following two-parameter equation

$$\log \frac{k}{k_0} = mY \quad (1)$$

where  $m$  is the substance parameter expressing the sensitivity of the rate of solvolysis to  $Y$  and  $Y$  is a measure of the ionization power of solvent (solvent constant). The application of this equation was successful for a surprisingly great number of solvents [24]. The main difference between the transition states of  $S_N1$  and  $S_N2$  solvolysis consists in the fact that the first one is very near to the ionic pair (I)



and involves, in principle, whole charges while the second one comprises the solvent which directly participates in the rate-determining reaction step and is a component of the transition state (II)



This state involves only partial charges which are much less concentrated because they are dissipated in a voluminous particle. Thus we may assume that the transition state of the  $S_N1$  solvolysis must be much more sensitive to ionization power of solvent owing to which the  $S_N1$  solvolysis must exhibit a greater value of  $m$ .

The course of solvolysis of the  $\sigma$  complexes of  $\text{Tl}^{3+}$  with olefins is shown in Fig. 1.

The results of regression analysis are given in Table 2. The mean value of the parameter  $m$  is 0.129 for  $\text{RCH}=\text{CH}_2$  alkenes, 0.250 for  $\text{R}^1\text{R}^2\text{C}=\text{CH}_2$  alkenes, and 0.554 for internal alkenes. The lower the value of  $m$ , the less is the transition state similar to ionic pair (I) and the reaction comes near to the  $S_N2$  mechanism by its character. In general, we may consider the value  $m=0.5$  to be the mechanistic borderline approximately [26]. Higher values indicate that the transition state

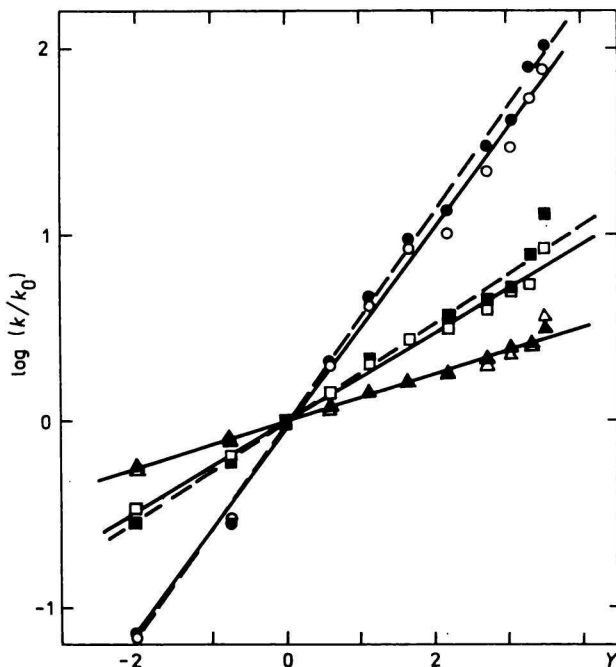


Fig. 1. Variation of the rate of solvolysis of the  $\sigma$  complexes with ionization power of the solvent at 25°C.

$k_0$  — Rate constant of the first-order solvolysis of the  $\sigma$  complex in a mixed solvent (80 v/v % of  $C_2H_5OH$  and 20 v/v % of  $H_2O$ ). Full lines represent graphical solution and dashed lines represent solution by means of a calculator.

○ ● Solvolysis of the  $\sigma$  complex of  $Tl^{3+}$  with 244TMP2 solved graphically or by means of a calculator;  
 □ ■ solvolysis of the  $\sigma$  complex of  $Tl^{3+}$  with 244TMP1 solved graphically or by means of a calculator;  
 △ ▲ solvolysis of the  $\sigma$  complex of  $Tl^{3+}$  with allyl alcohol solved graphically or by means of a calculator.

Table 2

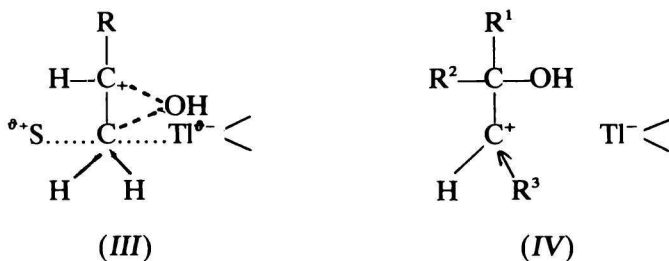
Regression analysis of the Grunwald—Winstein equation

$\sigma$ Complex of $Tl^{3+}$ with olefin	$m$ (graph/calc)	$r$ (graph/calc)	$S^*/\%$ graph/calc
Allyl alcohol	0.129/0.129	0.975/0.965	95.06/93.12
244TMP1	0.240/0.260	0.986/0.992	97.18/98.34
244TMP2	0.538/0.570	0.998/0.998	99.60/99.60

a)  $S = 100 r^2$ .

exhibits the character of ionic pair (*I*) while the transition state is only little or not at all similar to ionic pair at lower values of this parameter.

On the basis of experimental values of *m*, we may thus assume that the solvolysis of the  $\sigma$  complexes of  $Tl^{3+}$  with  $RCH=CH_2$  and  $R^1R^2C=CH_2$  alkenes obeys the  $S_N2$  mechanism and the transition state exhibits the character of species (*III*) while the solvolysis of the  $\sigma$  complexes of  $Tl^{3+}$  with internal alkenes might follow the  $S_N1$  mechanism and the transition state exhibits the character of species (*IV*)



The positive charge of the C atom in transition state (*IV*) may be stabilized by the electron-donating effect of the alkyl group  $R^3$ . Since the magnitude of positive charge on the central carbon atom in transition state (*III*) and (*IV*) is greater than in the fundamental state ( $\sigma$  complex), we may expect that the substituents able to stabilize positive charge by mesomeric or electron-donating inductive effect must accelerate the solvolysis.

The  $S_N1$  mechanism of solvolysis of internal alkenes could be responsible for a considerable decrease in reaction rate in case of the  $\sigma$  complex of  $Tl^{3+}$  with 244TMP2 (Table 1). An increase in concentration of ethanol reduces the solvation ability of reaction medium which results in a decrease in kinetic solvation effect (causing a reduction of energetic exertion requisite for the activation of reactants on account of decrease in solvation of the transition state [27]) and brings about a reduction of the rate of solvolysis.

## References

1. McKillop, A., *Pure Appl. Chem.* 43, 463 (1975).
2. McKillop, A. and Taylor, E. C., *Endeavour* 36, 88 (1976).
3. Strašák, M., *Chem. Listy* 72, 673 (1978).
4. Henry, P. M., *J. Amer. Chem. Soc.* 87, 990 (1965).
5. Henry, P. M., *J. Amer. Chem. Soc.* 87, 4423 (1965).
6. Henry, P. M., *Advan. Chem. Ser.* 70, 126 (1968).
7. Kabbe, H. J., *Justus Liebigs Ann. Chem.* 656, 204 (1962).
8. Pande, K. C. and Winstein, S., *Tetrahedron Lett.* 1964, 3393.

9. Uemura, S., Miyoshi, H., Toshimitsu, A., and Okano, M., *Bull. Chem. Soc. Jap.* 49, 3285 (1976).
10. Byrd, J. E. and Halpern, J., *J. Amer. Chem. Soc.* 95, 2586 (1973).
11. Strašák, M. and Majer, J., *Collect. Czech. Chem. Commun.*, in press.
12. Nadon, L., Tardat, M., Zador, M., and Fliszár, S., *Can. J. Chem.* 51, 2366 (1973).
13. Ouellette, R. J., Kordosky, G., Levin, Ch., and Williams, S., *J. Org. Chem.* 34, 4104 (1969).
14. Strašák, M. and Hrušovský, M., *J. Org. Chem.* 42, 685 (1977).
15. Strašák, M. and Hrušovský, M., *Collect. Czech. Chem. Commun.* 42, 3278 (1977).
16. Strašák, M., *React. Kinet. Catal. Lett.* 7, 387 (1977).
17. Strašák, M., *Z. Naturforsch.* 33b, 224 (1978).
18. Strašák, M. and Majer, J., *Tetrahedron Lett.* 1978, 5037.
19. Strašák, M., Hrušovský, M., Urbanec, J., Vojtko, J., and Greguš, Š., *Chem. Zvesti* 30, 553 (1976).
20. Korenman, I. M., *Analiticheskaya Khimiya Tallia*. Izd. Akad. Nauk SSSR, Moscow, 1960.
21. DeTar, D. F., *Comput. Chem.* 2, 39 (1978).
22. Hughes, E. D. and Ingold, C. K., *J. Chem. Soc.* 1935, 244.
23. Grunwald, E. and Winstein, S., *J. Amer. Chem. Soc.* 70, 846 (1948).
24. Bentley, T. W. and von Schleyer, P. R., *Advan. Phys. Org. Chem.* 14, 2 (1977).
25. Fainberg, A. H. and Winstein, S., *J. Amer. Chem. Soc.* 78, 2770 (1956).
26. Sykes, P., *Skúmanie mechanizmov organických reakcií*. (Investigation of Mechanisms of Organic Reactions.) P. 236. Alfa Publishers, Bratislava, 1978.
27. Plakhotnik, V. N. and Drabkina, A. Ch., *Kinet. Katal.* 18, 227 (1977).

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