# STRUCTURE EFFECTS IN OXIDATION OF ALIPHATIC KETONES BY THALLIUM(III) SULPHATE

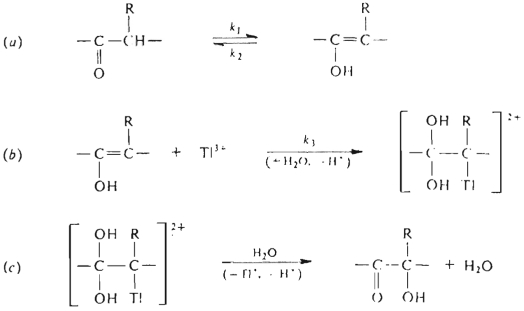
Miroslav PECHÁL[a] and Milan STRAŠÁK[b]

[a] *Shoe and Leather Research Institute, 762 65 Gottwaldov and*
[b] *Department of Analytical Chemistry, Faculty of Pharmacy,*
*Comenius University, 832 32 Bratislava*

Received June 21st, 1982

Oxidation kinetics of 11 aliphatic ketones ($R^1COR^2$) by thallium(III) sulphate in dilute sulphuric acid have been studied by UV spectrophotometry. The oxidation of methyl alkyl ketones ($R^2 > CH_3$) follows the first order kinetics, that of higher dialkyl ketones ($R^1, R^2 > CH_3$) obeys the second order kinetic equation. Polar and steric effects in the oxidation of aliphatic ketones have been separated by application of LFER to the chosen sets of methyl alkyl ketones ($R^2 > CH_3$) and dialkyl ketones ($R^1$, $R^2 > CH_3$). Structural factors have a certain effect on the oxidation rate of methyl alkyl ketones, the changes in the reaction rate being ascribable almost exclusively to steric effects of the $R^2$ substituents. The polar effects are very important in the oxidation of dialkyl ketones. Results of the application of LFER suggest that enol formation is the rate-determing step in the oxidations of the two sets of ketones.

So far, the oxidation kinetics of ketones by thallium(III) salts have been studied in few cases only[1-4]. The oxidation of aliphatic ketones is described by both the first order[1] and the second order kinetic equations[5]. We have found that oxidations



SCHEME 1

of methyl alkyl ketones ($R^2 > CH_3$) and dialkyl ketones ($R^1$, $R^2 > CH_3$) by thallium(III) sulphate in aqueous media follow the first order and the second order[6] kinetics, respectively. The mechanism consists of three subsequent steps[6,7]: (*a*) oxo-enol tautomeric equilibrium, (*b*) oxythallation, and (*c*) decomposition of oxythallic adduct.

α-Hydroxy ketone are final products of the oxidations of aliphatic ketones by thallium(III) ions in aqueous media[8]. Similarly, oxidation by thallium(III) acetate in acetic acid produces α-acetoxy ketones[1], and that by thallium(III) nitrate in acetonitrile produces α-nitrates of ketones[9].

So far, the reaction rate has been correlated with structure in oxidations of alkyl aryl ketones only[4]. The kinetic measurements[1-4,6] show that the oxidation rate of ketones is limited by the enolization rate. We tried to support this fact with the use of the linear free-energy relationship in the case of oxidation of aliphatic ketones by thallium(III) sulphate, too.

## EXPERIMENTAL

Thallium(III) sulphate solution was prepared by electrolytic oxidation of thallium(I) sulphate solution in dilute sulphuric acid[10]. The aliphatic ketones of at least 99·5% purity (chromatography) were obtained by known procedures[11], 4-Methyl-2-pentanone was obtained by rectification of a commercial product (VÚP Nováky).

The kinetic measurements were carried out by the method described earlier[6] using suitable concentrations for spectrophotometric technique: $[Tl^{3+}]_0 = 2{\cdot}91 \,.\, 10^{-4}$ mol $l^{-1}$, $[\text{ketone}]_0 = 2{\cdot}91 \,.\, 10^{-3}$ mol $l^{-1}$, and $[H_2SO_4] = 1 \,.\, 10^{-1}$ mol $l^{-1}$. The oxidation kinetics were followed by UV spectrophotometry (Specord UV VIS, Zeiss Jena) using the absorbance decrease due to decreasing $Tl^{3+}$ ion concentration which were determined as chlorothallium(III) complexes[12] at the wavelength 250 nm ($\varepsilon_3 = 3{\cdot}56 \,.\, 10^2$ $m^2$ $mol^{-1}$). Absorbance of chlorothallium(I) complexes is relatively low at this wavelength ($\varepsilon_1 = 1{\cdot}49 \,.\, 10^1$ $m^2$ $mol^{-1}$), that of the present organic compounds being negligible.

## RESULTS

Recently we have published[13] kinetic data of oxidation of aliphatic ketones ($R^1COR^2$) with thallium(III) sulphate: the first order rate constants $k_I$ of oxidation of methyl alkyl ketones ($R^2 > CH_3$) and the second order rate constants $k_{II}$ of the oxidation of dialkyl ketones ($R^1$, $R^2 > CH_3$). For qulitative evaluation of structure effects we used the classic Taft polar equation (*1*) as well as its modified steric form (*2*) and the combined four-parameter equation (*3*),

$$\log k = \log k_0 + \varrho^*\sigma^* , \qquad (1)$$

$$\log k = \log k_0 + \delta E_S , \qquad (2)$$

$$\log k = \log k_0 + \varrho^*\sigma^* + \delta E_S , \qquad (3)$$

where $k_0$ is a statistical quantity, $\sigma^*$ and $E_S$ are polar and steric substituent parameters, respectively, and $\varrho^*$ and $\delta$ are the reaction parameters. Validity of the given relations was verified in the both reaction series[13] with the model containing C=O bond as the reaction centre and $CH_3$ group as the standard substituent. Table I presents summary values of the substituent parameters of the ketones.

Figs 1 and 2 present influence of structure effects on the oxidation rate of methyl alkyl ketones and dialkyl ketones, respectively. Double linear regression analysis showed that the oxidation rate of methyl alkyl ketones can be expressed by Eq. (*4*) (R = 0·996) with sufficient reliability. Analogous equation for oxidation of dialkyl ketones cannot be formulated because of small number of members in this reaction series.

$$\log k_{\mathrm{I}} = 0{\cdot}358\sigma^* + 0{\cdot}594E_S - 4{\cdot}994 \qquad (4)$$

## DISCUSSION

According to the observed kinetic behaviour the investigated ketones can be divided into two groups[6]: the oxidation of methyl alkyl ketones ($R^2 > CH_3$) is described

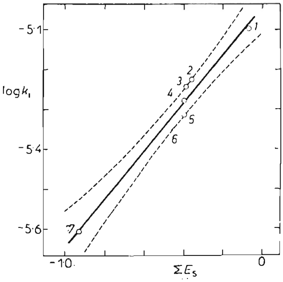


FIG. 1

The LFE-SE dependence for the oxidation of methyl alkyl ketones ($R^2 > CH_3$) by thallium(III) sulphate at 45°C. The full line corresponds to the real regression straight line, the dashed line represent the 97·5% reliability interval. For numbers see Table I. $\delta = +0{\cdot}603$, $R = 0{\cdot}968$, $S = 93{\cdot}7\%$

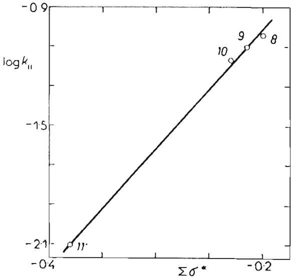


FIG. 2

The LFE-PE dependence for the oxidation of dialkyl ketones ($R^1$, $R^2 > CH_3$) by thallium(III) sulphate at 55°C. For numbers see Table I. $\varrho^* = 6{\cdot}031$, $R = 0{\cdot}999$, $S = 99{\cdot}7\%$

by kinetic equation of the first order (Eq. (*5*)), whereas that of dialkyl ketones ($R^1$, $R^2 > CH_3$) is described by the second order kinetic equation (Eq. (*6*)). The oxidation of acetone cannot be described by a kinetic equation of simple reaction[6]. As molar excess of ketone with respect to $Tl^{3+}$ was sufficient, the observed kinetic order was decreased by one degree.

$$-\mathrm{d}[\mathrm{Tl}^{3+}]/\mathrm{d}t = k_{\mathrm{I}}[\text{methyl alkyl ketone}] = k^{0}_{\mathrm{obs}} \tag{5}$$

$$-\mathrm{d}[\mathrm{Tl}^{3+}]/\mathrm{d}t = k_{\mathrm{II}}[\text{dialkyl ketone}]\,[\mathrm{Tl}^{3+}] = k^{\mathrm{I}}_{\mathrm{obs}}[\mathrm{Tl}^{3+}] \tag{6}$$

The kinetic data given in ref.[13] suggest that the oxidation rates of linear ketones are not much different and decrease with increasing branching of carbon chain at α and β positions. The only exception is the oxidation of 2-butanone in the first reaction series, its rate being somewhat higher than that of other linear methyl alkyl ketones. This finding agrees with results of ref.[16] dealing with determination of rate constants of enolization of aliphatic ketones, where similar mutual relation was observed in reactivities of tert-butyl alkyl ketones.

Validity of the isokinetic relation[17] in the given reaction series of the oxidation of aliphatic ketones was proved in ref.[13] where the temperature values 148 and 205 K were found for methyl alkyl ketones and dialkyl ketones, respectively. Similar

TABLE I

Values of the Taft polar ($\sigma^*$) and steric ($E_S$) constants for the aliphatic ketones ($R^1COR^2$) studied

| No | Ketone | $\sum\sigma^{*a}$ | $\sum E_S{}^b$ |
|---|---|---|---|
| 1 | 2-Butanone | −0·100 | −0·07 |
| 2 | 2-Pentanone | −0·115 | −0·36 |
| 3 | 2-Hexanone | −0·130 | −0·39 |
| 4 | 2-Heptanone | −0·160 | −0·40 |
| 5 | 2-Octanone | −0·160 | −0·40 |
| 6 | 3-Methyl-2-butanone | −0·190 | −0·47 |
| 7 | 4-Methyl-2-pentanone | −0·125 | −0·93 |
| 8 | 3-Pentanone | −0·200 | −0·14 |
| 9 | 3-Hexanone | −0·215 | −0·43 |
| 10 | 4-Heptanone | −0·230 | −0·72 |
| 11 | 2,4-Dimethyl-3-pentanone | −0·380 | −0·94 |

[a] The values $\sigma^*$ taken from ref.[14]; [b] the values $E_S$ taken from ref.[15].

to different kinetic behaviour of the two sets of ketones, the influence of structure effects on the reaction rate are different in the two reaction series, too. From Fig. 1 it is obvious that structure of ketone has a certain influence on the oxidation rate of methyl alkyl ketones, and the reaction rate changes can be ascribed exclusively to steric effect of the substituent, whereas according to Eq. (*1*) the kinetic data cannot be correlated. The found value of the reaction parameter ($\delta = +0.603$) corresponds well to the value $+0.542$ found for bromination of tert-butyl alkyl ketones[16] and to the value $+0.611$ calculated from kinetic data of oxidation of aliphatic ketones by thallium(III) acetate[1] involving enol formation as the rate-determining step. Also testing of significance of coefficients of proportionality of Eq. (*4*) shows that steric effects represent more significant factors in oxidation of methyl alkyl ketones, being able to explain about 89% of variability of the rate constants.

In the oxidation of dialkyl ketones (Fig. 2), influence of inductive effects of the substituents on the reaction rate is distinct ($\varrho^* = +6.031$), whereas that of steric effects is of less significance ($R = 0.735$). Positive values of the reaction parameters in the two series form an indirect support of our results of studies of the oxidation kinetics of ketones[6] and effect of salt concentration on the reaction rate[18] which suggested the enol formation as the rate-determining step. This fact represents an important difference with respect to the oxidation of alkenes by the same reagent[19], where the found values of the reaction parameters (for $RCH{=}CH_2$ alkenes $\varrho^* = -2.91$ and $\delta = -0.92$) suggest that oxythallation represents the rate-determining step in this reaction.

The results show that in the oxidation of ketones by thallium(III) sulphate (in contrast to analogous oxidation of alkenes[20]) the rate-determining step (enol formation) is identical with the product-determining step of the reaction.

## REFERENCES

1. Radhakrishnamurti P. S., Pati S. N.: Indian. J. Chem. *17A*, 97 (1979).
2. Littler J. S.: J. Chem. Soc. *1962*, 827.
3. Srinivasan P., Venkatasubramanian V. R.: Indian J. Chem. *14A*, 488 (1976).
4. Khandual N. C., Satpathy K. K., Nayak P. L.: Proc. Indian. Acad. Sci. *77A*, 163 (1973).
5. Meenakshi A., Santappa M: Indian J. Chem. *11A*, 393 (1973).
6. Pechál M., Vojtko J., Kuběna J., Hrušovský M.: React. Kinet. Catal. Lett. *20*, 151 (1982).
7. McKillop A., Hunt J. D.: J. Org. Chem. *37*, 3381 (1972).
8. Pechál M., Cvengrošová Z., Hrušovský M.: Chem. Prům. *31*, 525 (1981).
9. McKillop A., Young D. W., Edwards M., Hug R. P., Taylor E. C.: J. Org. Chem. *43*, 3773 (1978).
10. Strašák M., Hrušovský M., Urbanec J., Vojtko J., Greguš Š.: Chem. Zvesti *30*, 553 (1976).
11. Marko M., Krasnec Ľ.: *Základy preparativnej organickej chémie.* Štátne vydavatelstvo technickej literatúry, Bratislava 1962.
12. Korenman I. M.: *Analiticheskaya Khimiya Talliya.* Izd. Akad. Nauk SSSR, Moscow 1960.
13. Pechál M., Strašák M., Vojtko J., Hrušovský M.: React. Kinet. Catal. Lett. *20*, 157 (1982).

14. Taft R. W. in the book: *Steric Effects in Organic Chemistry* (M. S. Newman, Ed.), Chapter XIII. Wiley, New York 1956.
15. Welss P. R.: Chem. Rev. *63*, 171 (1963).
16. Dubois J. E., Toullec J.: Chem. Commun. *1969*, 292.
17. Brown R. F.: J. Org. Chem. *27*, 3010 (1962).
18. Pechál M., Holotík Š., Strašák M., Hrušovský M.: Chem. Zvesti, *37* 159 (1983).
19. Strašák M., Hrušovský M.: J. Org. Chem. *42*, 685 (1977).
20. Strašák M., Majer J.: J. Org. Chem. *45*, 3580 (1980).

Translated by J. Panchartek.