

# KINETICS OF THE REACTION OF *trans*-3-METHYLTHIOACRYLOPHENONE WITH HYDROXIDE ION. DETECTION OF CARBANION INTERMEDIATE BY THE DIFFERENCE SPECTRUM.\*

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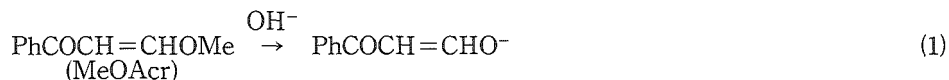
## SUMMARY

Reaction of *trans*-3-methylthioacrylophenone (MeSAcr) with hydroxide ion was followed spectrophotometrically in aqueous solution. The reaction was found to be a typical series reaction: MeSAcr → benzoylactaldehyde enolate → acetophenone.

A carbanion intermediate, the enolate ion, was detected by the coincidence of difference spectra between the spectra in basic reaction solutions and in their acidified solutions with those between the spectra of benzoylactaldehyde enolate and of the parent aldehyde. The first step of reaction in eq. (3) was kinetically first order in MeSAcr and first order in hydroxide ion. The second-order rate constants were obtained for MeSAcr-hydroxide ion combination reactions. The first-order rate coefficients for the second step of reaction in eq. (3) were obtained at the later stage of reaction where almost all MeSAcr was consumed. The rate coefficients are expressed as:  $k_{\text{obs}} = k_0 + k_{\text{OH}^-} [\text{OH}^-]$ . This is completely consistent with a mechanism for the hydrolysis of enolates of dicarbonyl compounds.

## Introduction

Kinetic studies have been reported<sup>1,2</sup> on the reaction of a series of nucleophiles with *trans*-3-methoxy- and *trans*-3-methylthio-acrylophenone derivatives (MeOAc and MeSAcr). While the reaction of MeSAcr with hydroxide ion has been found to be spectrally complex as shown in Figure 1, the one of MeOAc is spectrally simple as shown in Figure 2.



However, the latter reaction (1) at higher hydroxide concentrations is followed by a slower subsequent retro-aldol type reaction in equation (2).<sup>3</sup>

\* Dedicated to Professor Shougo Shikata in honour of his retirement.

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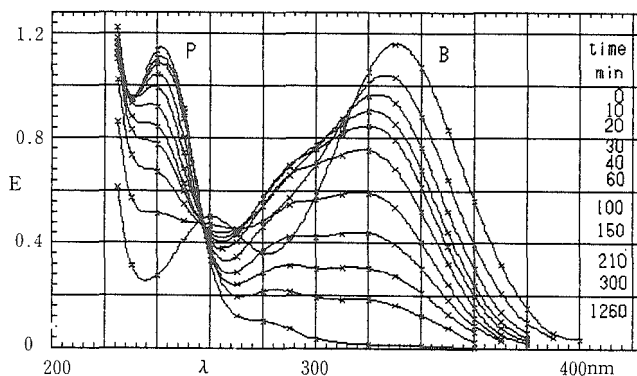


Figure 1. Reaction of MeSAcr (B:  $0.67 \times 10^{-4}$  M) with Hydroxide Ion (1.67 M) in Aqueous Solution at 25°. (B→P)

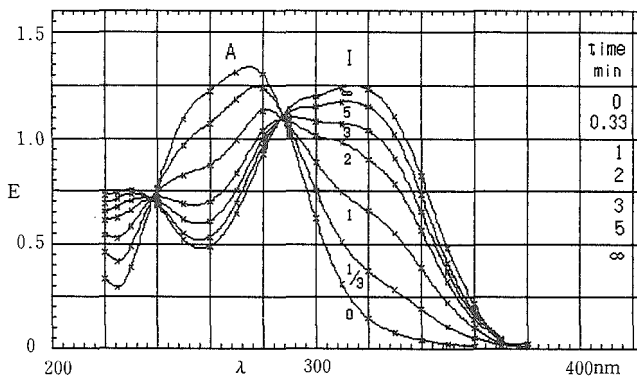
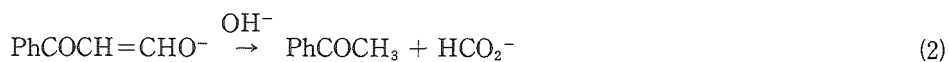
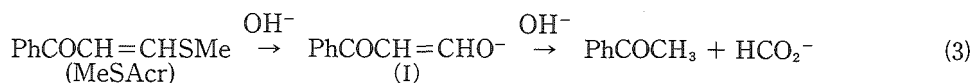


Figure 2. Reaction of MeOAc (A:  $1.0 \times 10^{-4}$  M) with Hydroxide Ion (0.0167 M) at 25°. I: Benzoylactaldehyde enolate (A→I)



At lower hydroxide ion concentrations, the second step of the reaction (2) is negligibly slow with MeOAc and is simple.<sup>3</sup>

The reaction with MeSAcr is much slower than with MeOAc. At higher concentrations of hydroxide ion, however, the reaction (2) for MeSAcr would be possible. The overall reaction with MeSAcr seems similarly to be a series reaction (3):



The UV spectra with MeSAcr and acetophenone, respectively, are almost same in acidic and basic solutions. But the spectrum with benzoylactaldehyde in acidic solution is very different from that in basic solution because of its enolate form (I). Formic acid and

formate ion have no appreciable absorption in longer wave lengths over 260 nm. Therefore, the intermediate enolate ion (I) can be detected by a difference spectrum between in acidic and basic solutions.

For the determination of rate constants for a step of complex reaction, analysis of the reaction is inevitable. The present paper concerns the spectrophotometric detection of a possible enolate intermediate for the reaction of MeSAcr with hydroxide ion. Kinetic studies indicate that the reaction should be a series one. Also, the paper involves determination of rate constants for the first step involving attack of hydroxide ion on MeSAcr, and for the second step involving retro-aldol type reaction.

### Results and Discussions

Detection of Carbanion Intermediate (I). At lower hydroxide ion concentration of 0.017 M, spectral change according to the reaction (1) is shown in Figure 2. The methoxyacrylophenone of absorption maximum at 278 nm was converted to benzoylacetalddehyde enolate ion (I) of absorption maximum at 315 nm. At higher hydroxide ion concentration of ca. 0.24 M, however, the reaction for MeOAc is different from the one at lower hydroxide ion concentration. As seen from Figure 3, conversion of MeOAc to the carbanion (I) was an instantaneous reaction, and was followed by a slower reaction of (I) into products of absorption maximum at 240 nm. The products are acetophenone and formate ion, in consistency with equation (2).

Spectra in basic solutions for MeSAcr and for acetophenone did not change appreciably on acidification with hydrochloric acid. But spectrum for benzoylacetalddehyde enolate ion in basic solution ( $\lambda_{\max}$  315 nm) changed remarkably on acidification ( $\lambda_{\max}$  240 nm). Therefore, a carbanion intermediate (I) for MeSAcr reaction can be detected by the spectral difference between in basic and acidified solutions during the reaction.

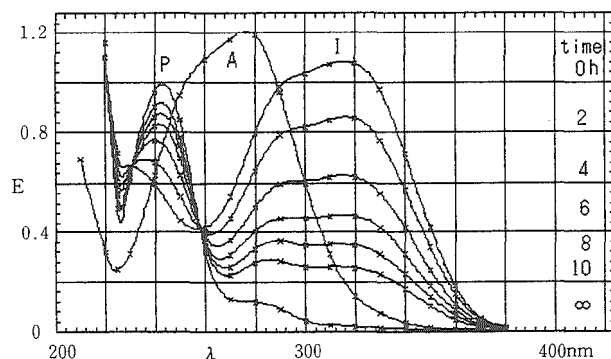
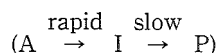


Figure 3. Consecutive Reaction of MeOAc (A : ca.  $0.95 \times 10^{-4}$  M) with Hydroxide Ion (ca. 0.24 M) at 25°.



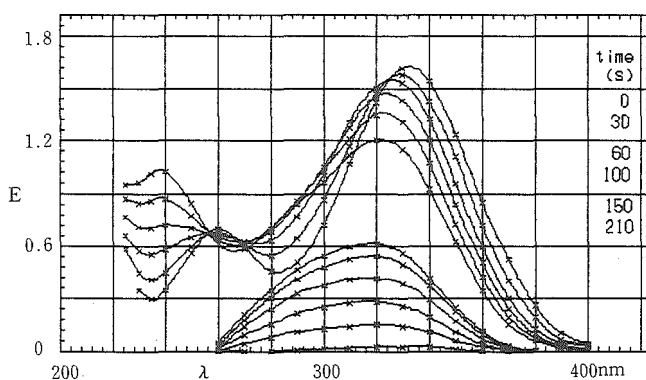


Figure 4. Reaction of MeSAcr ( $0.97 \times 10^{-4}$  M) with Hydroxide Ion (0.167 M).  
 Upper part : Change in spectrum during the reaction.  
 Lower part : Change in difference spectrum (Detection of the Carbanion). Reaction time : from the bottom 1, 31, 61, 101, 151, 211 min.

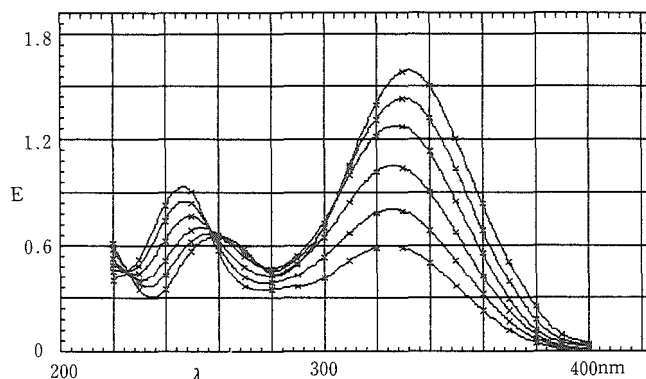
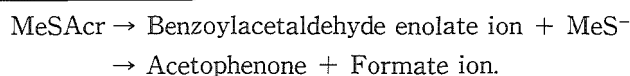


Figure 5. Reaction of MeSAcr ( $0.97 \times 10^{-4}$  M) with Hydroxide Ion (0.167 M). Spectra of Acidified Solution.

Changes in spectra for the reaction are shown in Figure 4 (upper part) in basic solutions and in Figure 5 in acidified solutions. The difference spectra between Figure 4 and Figure 5 are also shown in Figure 4 (lower part). The difference spectrum has an absorption maximum at 320 nm, which is in consistency with that of the difference spectrum between the spectra of benzoylacetalddehyde enolate and of the parent aldehyde. At first the absorbance increased with increasing time, and then it decreased through the maximum. This is evidence for the carbanion intermediate (I) in reaction scheme (3).

Analysis of the Reaction. The reaction is surely a series reaction (3):



The spectra of these components are shown in Figure 6, where P denotes products in hydroxide solution including thiomethoxide ion. Since these spectra are different from

each other, the analysis of components can be attained by three-point analysis.<sup>5</sup> For the analysis absorbances at 240, 290, and 350 nm were utilised.

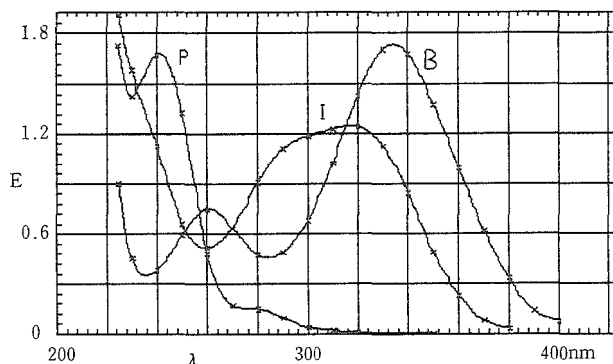


Figure 6. UV Spectra of MeSAcr (B), Benzoylactaldehyde enolate Ion (I), and Acetophenone+Formate Ion (P) in  $0.67 \times 10^{-4}$  M Solutions.

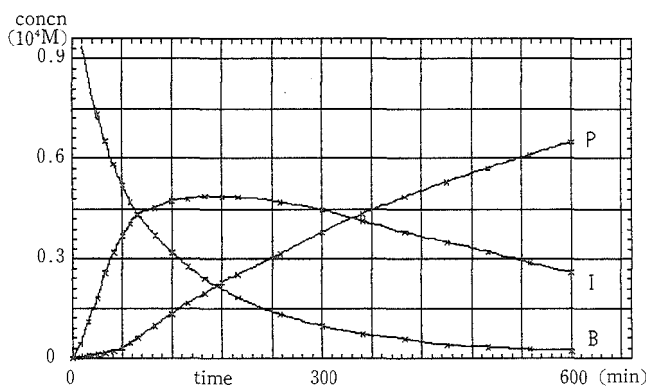


Figure 7. Conversion Curve for Reaction of MeSAcr ( $0.93 \times 10^{-4}$  M) with Hydroxide Ion (0.25 M) in Aqueous Solution at  $25^\circ$ .

The reactions in aqueous solution were followed spectrophotometrically. The results, obtained by three-point analysis, are shown in Figure 7. At first, the carbanion intermediate increased as MeSAcr decreased, and then decreased gradually through a maximum. The final products, acetophenone and formate ion, increased gradually after a short time lag. Therefore, the reaction is a typical consecutive one, in consistency with scheme (3).

Kinetics. The first step of reaction is first-order in MeSAcr and first-order in hydroxide ion. The second order rate constants, obtained by the division of first-order rate coefficients with hydroxide ion concentrations, have a good constancy as shown in Table 1. The value of  $k_2 = (5.3 \pm 0.2) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ .

Observed rate coefficients for the second step are shown in Table 2, and expressed

Table 1. RATE CONSTANTS FOR THE FIRST STEP OF REACTION OF MeSAcr WITH HYDROXIDE ION IN AQUEOUS SOLUTION AT 25°.

[MeSAcr]/M	[OH <sup>-</sup> ]/M	$k_{\text{obs}}/\text{s}^{-1}$	$k_2/\text{M}^{-1}\text{s}^{-1}$
$0.667 \times 10^{-4}$	1.0	$5.15 \times 10^{-4}$	$5.2 \times 10^{-4}$
$0.667 \times 10^{-4}$	1.0	$5.07 \times 10^{-4}$	$5.1 \times 10^{-4}$
$0.733 \times 10^{-4}$	0.75	$4.03 \times 10^{-4}$	$5.4 \times 10^{-4}$
$0.833 \times 10^{-4}$	0.50	$2.71 \times 10^{-4}$	$5.4 \times 10^{-4}$
$0.833 \times 10^{-4}$	0.50	$2.60 \times 10^{-4}$	$5.2 \times 10^{-4}$
$0.933 \times 10^{-4}$	0.25	$1.43 \times 10^{-4}$	$5.7 \times 10^{-4}$

Av.  $(5.3 \pm 0.2) \times 10^{-4}$ 

Table 2. RATE CONSTANTS FOR THE SECOND STEP OF REACTION OF MeSAcr WITH HYDROXIDE ION IN AQUEOUS SOLUTION AT 25°.

[MeSAcr]/M	[OH <sup>-</sup> ]/M	$k'_{\text{obs}}/\text{s}^{-1}$
$0.667 \times 10^{-4}$	1.0	$8.2 \times 10^{-5}$
$0.733 \times 10^{-4}$	0.75	$7.1 \times 10^{-5}$
$0.833 \times 10^{-4}$	0.50	$6.1 \times 10^{-5}$
$0.933 \times 10^{-4}$	0.25	$5.1 \times 10^{-5}$

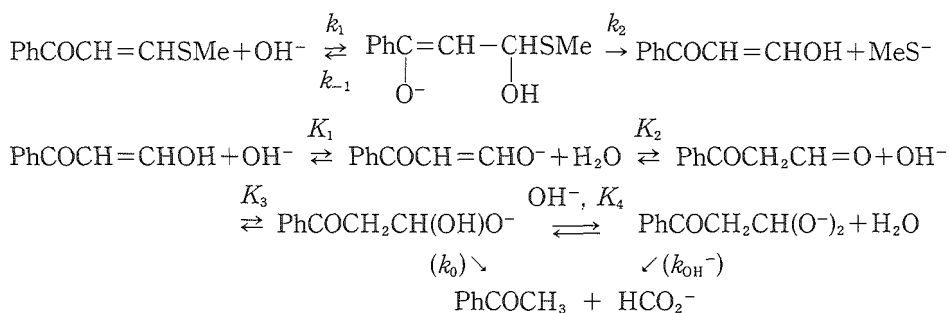
$$k'_{\text{obs}} = 4.1 \times 10^{-5} + 4.1 \times 10^{-5} [\text{OH}^-] \text{ s}^{-1} \quad (r=1.000)$$

as :

$$k_{\text{obs}} = k_0 + k_{\text{OH}^-} [\text{OH}^-] \quad (4)$$

Here, an excellent correlation ( $r=1.000$ ) was obtained. The kinetic situation in eq. (4) is completely consistent with that for the alkaline hydrolysis of  $\beta$ -dicarbonyl compounds.<sup>3,4</sup> Since benzoylactaldehyde exists as an enolate ion under the present conditions, the mechanisms are shown in the following scheme<sup>2,3</sup>.

Scheme



The observed second-order rate constants for the first step can be expressed as  $k_{\text{obs}} = k_1 k_2 / (k_{-1} + k_2)$  employing the steady state approximation. Since thiomethoxide ion is a much better leaving group than methoxide ion,  $k_2 \gg k_{-1}$ . Hence,  $k_{\text{obs}} = k_1$ . Rate-

determining step for the first step is attack of hydroxide ion on MeSAcr.

The second step involves rate-determining cleavage of both mono- ( $k_0$  term) and dianions ( $k_{OH}$  term) of benzoylactaldehyde hydrate,<sup>3</sup> as shown in Scheme.

## Experimental

Materials. *trans*-3-Methoxyacrylophenone (MeOAc) and *trans*-3-methylthioacrylophenone (MeSAcr) were prepared according to the following procedures. Benzoyl chloride was treated with chloroethene and anhydrous aluminium trichloride (by the Friedel-Crafts reaction) to form 3-chloroacrylophenone in a yield of 83%. B. p. 126-127°/20mmHg (lit.<sup>6,7</sup> 124°/12mmHg). The 3-chloroacrylophenone was treated with methoxide ion in methanol to form 3,3-dimethoxy-1-phenyl-1-propanone in a yield of 86%. Repeated distillation of the ketone from a small amount of dried sodium bisulphate gave MeOAc in a yield of 77%. B. p. 119-120°/4mmHg (lit.<sup>2</sup> 113-5°/0.5mmHg). *trans*-3-Methylthioacrylophenone was obtained in a yield of 56% by the reaction of 3-chloroacrylophenone with sodium thiomethoxide in methanol. Distillation over dried sodium bisulphate gave pure material. B.p.151-3°/6mmHg (lit.<sup>2</sup> 143-4°/0.7mmHg). The IR and NMR spectra of these substances are consistent with earlier data<sup>2</sup>.

Apparatus. A Shimadzu spectrophotometer Model UV-300, equipped with a Shimadzu spectral data processor SAPCOM-1, an NF digital storage oscilloscope DS-332, and a rapid mixing device, was utilised for the determination of the UV spectra. The cell compartment was thermostated at 25.0°±0.1°C.

IR spectra were recorded on a Hitachi spectrophotometer Model IR-260-10. NMR spectra were recorded on a JEOL FT90Q spectrometer with CDCl<sub>3</sub> as an internal standard.

Detection of Intermediate. For the detection of enolate intermediate the reaction was started on addition of an adequate volume of aqueous NaOH solution (3M) to the aqueous MeSAcr solution (10<sup>-4</sup>M) in a three-necked flask, thermostated at 25°. At the intervals of every 15 or 30 minute, the aliquots (3.0cm<sup>3</sup>) were pipetted out into a cell in the spectrophotometer. As soon as the spectrum was recorded and stored at the data processor, the solution in the cell was acidified on addition of concd. HCl (0.1cm<sup>3</sup>). The spectrum in acidic solution was recorded and stored analogously. The difference between these spectra in basic and acidic solutions was recorded as output from the data processor. These difference spectra are shown at the lower part of Figure 4. Time lag between the measurements in basic solution and in acidified solution was only one minute, while the reaction does not proceed so much during the time lag.

Kinetics. The reaction was started in the cell compartment on addition of potassium hydroxide solution (3M) to the MeSAcr or MeOAc solution (10<sup>-4</sup>M). Spectra during the reactions were monitored automatically at a constant interval of time set. The concentrations of the components vs time were obtained by three-point analysis of the spectra, as

shown in Figure 7. Three-point analysis is based on the following equations :

$$E_{240} = \epsilon_{a240}C_a + \epsilon_{b240}C_b + \epsilon_{c240}C_c$$

$$E_{290} = \epsilon_{a290}C_a + \epsilon_{b290}C_b + \epsilon_{c290}C_c$$

$$E_{350} = \epsilon_{a350}C_a + \epsilon_{b350}C_b + \epsilon_{c350}C_c$$

Here, E's denote extinctions at wave lengths subscript,  $\epsilon$ 's molar absorptivities of a (methylthioacrylophenone), b (benzoylacetalddehyde enolate), and c (acetophenone, formate ion, and thiomethoxide ion) components, and c's concentrations of the components. Molar absorptivities  $\epsilon_{a240}$ ,  $\epsilon_{b240}$ ,  $\epsilon_{c240}$ ,  $\epsilon_{a290}$ ,  $\epsilon_{b290}$ ,  $\epsilon_{c290}$ ,  $\epsilon_{a350}$ ,  $\epsilon_{b350}$ , and  $\epsilon_{c350}$  used are  $3.72 \times 10^3$ ,  $11.2 \times 10^3$ ,  $17.2 \times 10^3$ ,  $4.83 \times 10^3$ ,  $11.0 \times 10^3$ ,  $0.96 \times 10^3$ ,  $13.7 \times 10^3$ ,  $4.86 \times 10^3$ , and 0, respectively. (See Figure 6)

The apparent first-order rate constants for the first step were obtained by the least square method from logarithmic plots of the concentrations of MeSAcr vs time. Data are in Table 1. The apparent first order rate coefficients for the second step were obtained by the least square method from logarithmic plots of the concentrations of the enolate vs time at a later stage of reaction. The data are in Table 2.

### References

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