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CHEMISTRY OF SELENOPHENE

LVI. Kinetics of Mercuration of Selenophene Series Compounds*

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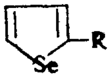
A study is made of the kinetics of mercuration of selenophene, 2-bromo-, 2-acetyl-, 2-ethoxycarbonyl, and 2-nitro-selenophene. Selenophene derivatives mercurate 1.5–3 times faster than the corresponding thiophene ones. The Hammett equation and the σ^+ constant give a good description of the effects of substituents in the selenophene ring on rate of mercuration. The aromaticity sequence for 5-membered heterocyclic ring compounds and benzene is furan > selenophene > thiophene > benzene.

Investigation of the kinetics of solvolysis of thiophene and selenophene series chloromethyl compounds led us to conclude that selenophene should undergo electrophilic substitution rather more readily than thiophene [1].

To check this we investigated the kinetics of mercuration of selenophene and its derivatives with mercuric acetate in glacial acetic acid, i.e., the kinetics of an electrophilic substitution reaction [2], for selenophene, 2-bromo-, 2-acetyl-, 2-ethoxycarbonyl-, and 2-nitroselenophene.

Table 1

Rate Constants and Arrhenius Equation Parameters for the Mercuration of 2-Substituted Selenophenes



R	K, l, mole^{-1} · min^{-1}					E kcal/mole	lg PZ
	25	35	50	75	90		
Br	0.704	1.97	4.0	—	—	14.1	10.13
$COOC_2H_5$	$3.72 \cdot 10^{-3}$	$8.0 \cdot 10^{-3}$	$2.8 \cdot 10^{-2}$	—	—	15.1	8.57
$COCH_3$	$2.33 \cdot 10^{-3}$	$6.87 \cdot 10^{-3}$	$3.9 \cdot 10^{-2}$	—	—	20.97	12.66
NO_2*	$1.55 \cdot 10^{-4}$	$4.12 \cdot 10^{-4}$	$2.11 \cdot 10^{-3}$	$1.47 \cdot 10^{-2}$	$4.3 \cdot 10^{-2}$	18.2	9.46

* The 2-nitroselenophene constants for 25°, 35°, and 50° C are calculated from the results obtained at higher temperatures.

In 1957 Japanese authors investigated a similar reaction for thiophene and its derivatives [3]. We investigated the kinetics of mercuration for the selenophene series under like conditions, and obtained data regarding the reactivities of selenophene and its derivatives in marked contrast to existing data for thiophene and its derivatives. On checking our method we obtained a rate constant for the mercuric acetate mercuration of thiophene in glacial acetic acid at 25° C (1.7 ± 0.2 l · mole^{-1} · min^{-1}) in good agreement with the Japanese authors' values (1.54 l · mole^{-1} · min) which showed that it was possible to obtain reliable results for comparison.

The method of investigating the kinetics is based on titrating unreacted mercuric acetate with potassium thiocyanate in the presence of iron ammonium alum as an indicator. The kinetics of mercuration of selenophene and its derivatives were investigated at 25°, 35°, and 50° C, but because 2-nitroselenophene mercurates very slowly even at 50° C, reaction was studied at 75° and 90° C.

Up to 20% mercuration the kinetics of the reaction for selenophene derivatives are well described by an equation for a second order reaction, but the reaction is slowed down when it proceeds to a greater extent, and apparently this is due to the reverse process. In the separate kinetic experiments for each of the compounds studied, the mercuration

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*For Part LV see [1].

velocity constants did not vary by more than 10%. The Arrhenius equation parameters were calculated from the data. Table 1 gives the results. E values are given with an accuracy of ±0.75 kcal/mole, and lg PZ values with an accuracy of ±1.

Table 2

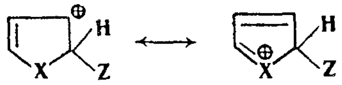
Mercuration Rate Constants for 2-Substituted Selenophenes and Thiophenes at 35° C

	K, $l \cdot mole^{-1} \cdot min^{-1}$			
	H	CH_3CO	$COOC_2H_5$	Br
Selenophenes	>20	$6.87 \cdot 10^{-3}$	$8.0 \cdot 10^{-3}$	1.97
Thiophenes	1.54	$3.73 \cdot 10^{-3}$	$4.81 \cdot 10^{-3}$	0.566
K selen./ K thioph.	>10	1.85	1.67	3.4

Since the mercuration of selenophene was very fast, its rate constant could not be determined accurately, clearly showing that selenophene mercurates considerably faster than thiophene.

Table 2 compares the mercuration rate constants for 2-substituted selenophenes with the results of the Japanese authors for the analogous 2-substituted thiophenes at 35° C.

The data of Table 2 show that selenophene derivatives with electron-accepting substituents, mercurate 1.5–3 times faster than the corresponding thiophene ones. This result indicates that a transition state stabilization of the positive charge according to the equation



is effected more easily on the selenium hetero-atom, than on the sulfur one.

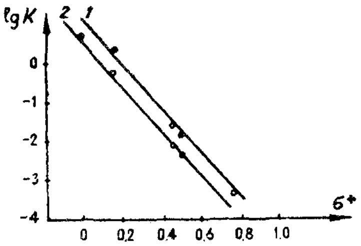


Fig. 1. Relationship between log(rate constant) for mercuration of 2-substituted selenophenes (1) and thiophenes (2) and σ^+, at 35° C.

It was of interest to ascertain whether the present results obeyed the Hammett equation. Data [3] show that logarithms of rate constants for mercuration of 2-substituted thiophenes are well described by the equation, but it is unclear what the constants used for the substituents were. We correlated our log(rate constant) values for the mercuration of 2-substituted selenophenes with Brown's σ^+ constants [4], usually used for correlating electrophilic substitution rate constants. For 2-acetylselenophene we used Hammett's constant σ^P, since for electron accepting substituent, σ^+ is practically the same as Hammett's σ^P. The value of the σ^+ constant which we recently [1] gave for the acetyl group, + 0.27, and which was obtained in a study of the solvolysis of 5-acetyl-2-chloromethylselenophene, obviously cannot be used for electrophilic substitution.

At all the temperatures used, the logarithm of the rate constant was found to exhibit a good linear relationship with σ^+. The correlation coefficient were 0.989 at 25° C, 0.986 at 35° C, and 0.987 at 50° C. For comparison with the results of [3], we plotted a graph of the relationship between log (rate constant) for mercuration of 2-substituted thiophenes and σ^+ at 36° C. The correlation coefficient for the resultant straight line was 0.991.

Figure 1 compares the Hammett straight lines for mercuration of 2-substituted thiophenes and selenophenes at 35° C. The two straight lines are practically parallel, ρ for the selenophenes is − 5.80, and for the thiophenes − 5.86. The parallel natures of the straight lines obtained show that transmission of electronic effects of substituents to a reaction center through the heterocyclic ring, and hence via the heteroatom, is effected in the same way for thiophene and selenophene.

The high ρ values for mercuric acetate mercuration in glacial acetic acid of 2-substituted selenophenes (− 5.77 at 25°, − 5.80 at 35° C, and − 5.14 at 50° C) and of 2-substituted thiophenes (− 5.86 at 35° C and − 5.60 at 50° C) indicate the great sensitivity of this reaction to electronic effects and the considerable ease of transmission of the latter through the selenophene and thiophene rings.

It was not possible to investigate the kinetics of mercuration of furan series compounds under the above conditions because of their rapid decomposition, which started when the reactants were mixed.

Thus we obtained direct confirmation of the hypothesis previously advanced, that selenophene undergoes electrophilic substitution more readily than thiophene. Our results show that in degrees of aromaticity, selenophene somewhat exceeds thiophene. Our recent results on comparison of aromaticities of selenophene and thiophene by Gilman's method agree with this; we found that when di(2-thienyl) di(2-selenienyl lead was decomposed with hydrogen chloride, twice as much selenophene as thiophene separated [5].

Thus from comparison of solvolysis rates for furan, thiophene, and selenophene chloromethyl compounds, and of rates of mercuration of thiophene, selenophene, and their derivatives, we construct the following sequence of decreasing degree of aromaticity for these heterocyclic rings furan > selenophene > thiophene > benzene.

Experimental

Reagents. The solvent was glacial AcOH (CP) which was frozen twice, and parts of the same stock used in all the runs. $HgOAc_2$ (medical) was twice recrystallized from water. KCNS (CP) was vacuum-dried for 1 hr at 10 mm and 150° C, then for 10 min at 200° C. HNO_3 (AR) and iron ammonium alum (AR) were used without further purification.

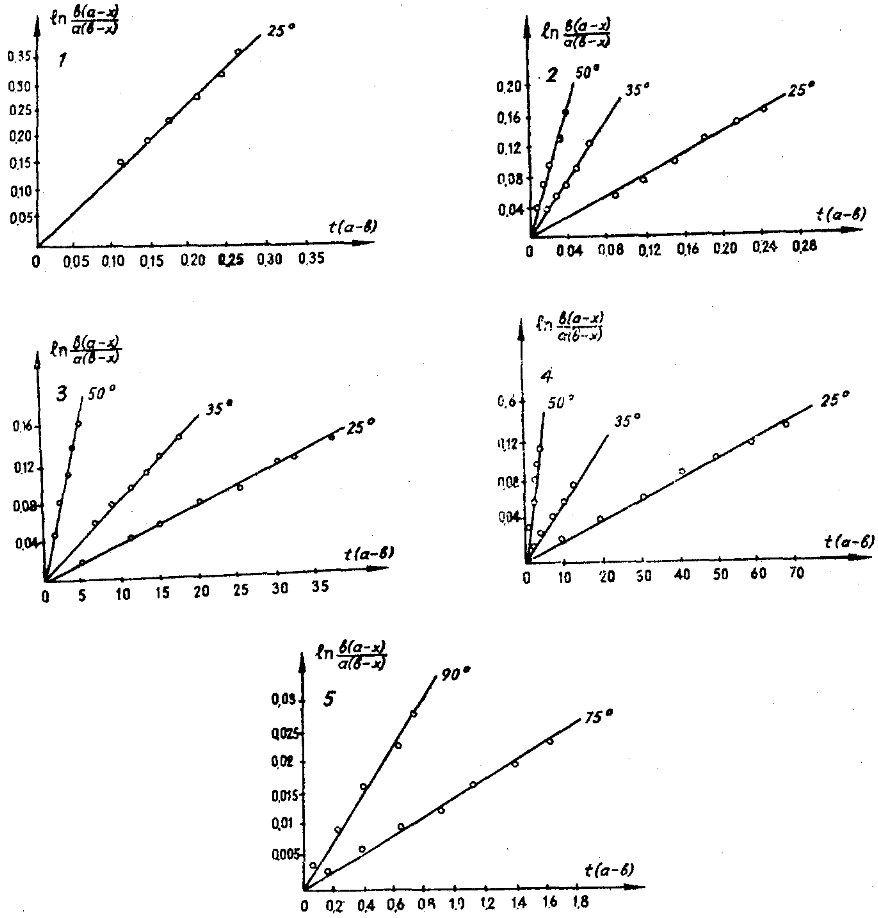


Fig. 2. Relationship between ln b(a−x)/a(b−x) and t(a−b) for mercuration of thiophene (1) 2-bromoselenophene (2), 2-ethoxycarbonylselenophene (3), and 2-acetylselenophene (4), and 2-nitroselenophene (5), at different temperatures.

Thiophene (pure) was distilled through a 30 theoretical plate column, when it had the following properties: bp 84.1° C, n_D^{20} 1.5284, d_4^{20} 1.5284, d_4^{20} 1.0637. The literature gives [6] 84.2° C, n_D^{20} 1.5287, d_4^{20} 1.0640. Selenophene was twice redistilled over Na, bp 110° C, n_D^{20} 1.5640, d_4^{20} 1.5247. The literature [7] gives 110.2°-110.7° C, n_D^{20} 1.5642, d_4^{20} 1.5251. 2-Bromoselenophene, bp 50.5° C (7 mm), n_D^{20} 1.6346, d_4^{20} 2.1014. The literature gives [8] 59° C (13 mm), n_D^{20} 1.635. 2-Acetylselenophene, bp 102° C (10 mm), n_D^{20} 1.5910, d_D^{20} 1.5431. The literature gives [9] bp 102° C (10 mm), n_D^{20} 1.5918, d_4^{20} 1.544. 2-Ethoxycarbonylselenophene, bp 99°-100° C (11 mm), n_D^{20} 1.5548, d_4^{20} 1.4790. The literature gives [10] bp 106°-107° C (14 mm), n_D^{20} 1.5525, d_4^{20}, 1.4765. 2-Nitroselenophene, bp 33.6°-33.9° C. The literature gives [11] bp 33.5°-34° C.

Procedure. A ml 100 conical flask was placed in a thermostat, and into it measured a quantity of mercuric acetate solution of known concentration in acetic acid, and a solution of the heterocyclic compound, at a precisely known concentration in acetic acid too. The ratio of the reactants taken was such that the concentration of the mercuric acetate in the reaction mixture was 0.004–0.03 mole/l, and the concentration of heterocyclic compound was 0.03–0.1 mole/l. The solutions of the reagents were previously kept for 15–20 min in the thermostat at the run temperature, which was held to ±0.1° C, then taken out with a calibrated pipet, and transferred to the reaction flask.

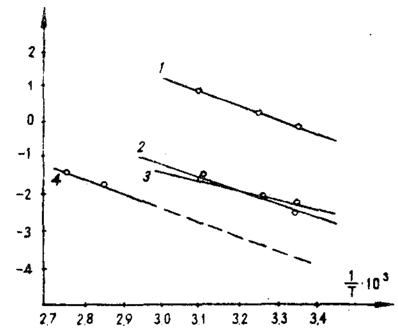


Fig. 3. Rate constants of mercuration of 2-bromoselenophene (1), 2-acetylselenophene (2), 2-ethoxycarbonylselenophene (3), and 2-nitroselenophene (4) as a function of temperature.

Aliquots (1–2 ml) were removed after definite times, and quickly run into 20 ml ice-water containing 1 ml concentrated HNO_3 and 5–7 drops of a saturated solution of the indicator, then rapidly titrated from a micro-burat with 0.05 N aqueous KCNS till a pale-yellow color appeared. Where reaction was fast, the reagents were mixed in the titrating flask. After a definite time the reaction was quenched by adding 20 ml ice-water containing HNO_3 and indicator, and the mixture quickly titrated.

Special runs showed that mercuric acetate concentration remained constant after the reaction mixture was mixed with ice-water.

In each run the mean value for the rate constant was found graphically as the tangent of the slope angle of the straight line plot of $\ln b(a-x)/a(b-x)$ against $t(a-b)$. Fig. 2. gives plots for all the compounds investigated at the various temperatures.

Fig. 3. shows that there was a good linear relationship between mercuration rate constants and the reciprocal of the temperature.

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