EQUILIBRIUM AND KINETIC ACIDITIES OF THIOPHENE AND SELENOPHENE

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UDC 541.45'127:547.732'739.3

Acid-base properties are one of the most important characteristics of reactivities. The determination of the strengths of CH acids by measuring their kinetic and equilibrium acidities is therefore of great interest (see [1, 2]).

The kinetic acidities of the five-membered heterocycles thiophene and selenophene were first established in [3-5]. It was shown that the rate constant for dedeuteration of the α-CD bond of selenophene is only 1.5 times higher than that of thiophene [exchange with $(CH_3)_2SO$ + tert-C_4H_9OLi], or else theyare practically identical (exchange with tert-C_4H_9OH + $CH_3OC_2H_4OC_2H_4OCH_3$ + tert-C_4H_9OK). However, the rate constant for deuterium exchange of the α-CH bonds of thiophene with liquid ND_3 is close to that for the CH group of triphenylmethane. Since data on the equilibrium acidities of five-membered heterocycles are not available, we set out to determine them by means of a spectrophotometric variant of the method of competitive metallation. We were able to simultaneously measure both the rate constants of the metallation of C_4H_4S and C_4H_4Se by triphenylmethyllithium, i.e., we were able to determine their kinetic acidities by a different method than that used in [3-5].

$$(C_6H_5)_3CLi + C_4H_4S\,(C_4H_4Se) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (C_6H_5)_3CH + C_4H_3LiS\,(C_4H_3LiSe) \tag{1}$$

The kinetics and equilibrium of reversible reaction (1) were studied in tetrahydrofuran (THF) at 25°C. The $(C_6H_5)_3CLi$ solutions were prepared by the action of n-C_4H_9Li on $(C_6H_5)_3CH$ in THF. The unchanged reagents were removed. A check established that the $(C_6H_5)_3CLi$ solutions in THF are quite stable with time. All of the operations were accomplished at high vacuum. The reaction was carried out in a sealed device (without stopcocks) equipped with a quartz cuvette and a firing pin for breaking the ampules containing weighed samples of $(C_6H_5)_3CH$ and C_4H_4CS (or C_4H_4Se). The starting $(C_6H_5)_3CLi$ concentrations ranged from 1 to 5 · 10^{-3} M, the starting $(C_6H_5)_3CH$ concentrations varied from 2 to 20 · 10^{-3} M, and the starting C_4H_4S (or C_4H_4Se) concentrations ranged from 5 to 20 · 10^{-3} M. The equilibrium of the forward metallation reaction was achieved after 200-400 h, while the equilibrium of the reverse reaction was established after 30-50 h. The rate constants of the forward (k_1) and reverse (k_{-1}) reactions were calculated from the equation for a reversible bimolecular reaction. We determined the extinction coefficient of $(C_6H_5)_3CLi$ in THF (ε = 2.8 · 10^4 liter/mole-cm) in order to calculate the equilibrium constants [$K_{e(f)}$ and $K_{e(r)}$].

Thiophene

$K_{e(f)}$	0,2	0,2	0,2	0,4	0,5	0,5	0,5
$K_{e(r)}$	0,3	—	—	—	0,5	—	—
$k_1 \cdot 10^4$, l/mole-sec	1,2	—	1,1	1,6	—	1,4	1,4
$k_{-1} \cdot 10^4$, l/mole-sec	8	—	6	4	—	3	3

Selenophene

$K_{e(f)}$	0,2	0,3	0,2	0,5	0,3	0,5	0,4
$K_{e(r)}$	—	0,6	0,4	0,9	0,5	—	—
$k_1 \cdot 10^4$ l/mole-sec	1,9	1,8	2,2	2,1	1,7	—	—
$k_{-1} \cdot 10^4$ l/mole-sec	11	7	9	4	5	—	—

The considerable scatter in the K_e and k_{-1} values is apparently associated with side reactions that show up in such prolonged experiments, particularly in the results of the calculation of $K_{e(r)}$, whose values

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are higher than the corresponding $K_{e(f)}$ values in all cases. The average $K_{e(f)}$ value for thiophene is 0.3 ∓ 0.1 and $k_1 = (1.3 \mp 0.2) \cdot 10^{-4}$ liter/mole-sec. For selenophene, $K_{e(f)} = 0.4 \mp 0.1$ and $k_1 = (1.9 \mp 0.2) \cdot 10^{-4}$ liter/mole-sec. Thus, judging from the results that we obtained, the concentration equilibrium acidities of thiophene and selenophene are almost identical and not much lower than those for $(C_6H_5)_3CH$. The kinetic acidities of these heterocycles, determined during their metallation, are also close in magnitude; the kinetic acidity of selenophene is somewhat higher than that of thiophene. The results of this study consequently are, on the whole, in agreement with the data on the relative acidities of both heterocycles, previously obtained in [3-5] by deuterium exchange. If the value pK = 31.48 from [6] is taken as arbitrary for the concentration equilibrium acidity of $(C_6H_5)_3CH$, the corresponding pK values for thiophene and selenophene will be 32.0 ∓ 0.2 and 31.8 ∓ 0.2, respectively. Our attempt to determine the acidity of furan relative to diphenylmethane was not successful, since $(C_6H_5)_2CHLi$, in contrast to $(C_6H_5)_3CLi$, reacts appreciably with THF. According to our observations, $(C_6H_5)_3CCs$ does not metallate thiophene in cyclohexylamine, i.e., a differentiating effect is apparently manifested.

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