Chemistry

T. A. KUDRYAVTSEVA, N. M. CHIRKOV, N. K. KOCHETKOV

1963

SovietRxiv

Abstract

Full Text

Chemistry

T. A. KUDRYAVTSEVA, N. M. CHIRKOV, N. K. KOCHETKOV

KINETICS OF THE REACTION OF SUBSTITUTION OF CHLORINE ATOMS IN SOME ARYL-β-CHLOROVINYL KETONES

(Presented by Academician V. N. Kondrat' ev, 1 VIII 1962)

Kinetic studies carried out earlier in our laboratory on the reaction of exchange of a halide atom under the action of a nucleophilic reagent, situated at a double bond in the system R—CO—CH = CHCl ($^{1-3}$), showed that the reactivity of the halide atom, in addition to the nature of the attacking nucleophilic reagent, depends to a great extent on the character of the carbonyl group located in the β-position to the halide atom. Thus, the activation energy of the substitution reaction is highest for salts of β-chlorocrotonic acids (R = ONa (21.3)), somewhat lower for esters of these acids ($R = OC_2H_5; OCH_3; OC_3H_7$, etc. (17.6)), and still lower for phenyl-β-chlorovinyl ketones ($R = C_6H_5$ (11)).

Since kinetic data on the nucleophilic substitution of a halide atom situated at a double bond are almost absent from the literature, despite the obvious interest of this question from the standpoint of understanding the reaction mechanism, we studied the kinetics of exchange of the halide atom in several aryl-β-chlorovinyl ketones having substituents in the phenyl nucleus, hoping thereby to clarify the influence of these substituents on the reaction rate. For the study we chose the reaction of an aryl-β-chlorovinyl ketone with sodium ethoxide in absolute alcohol. This reaction, as is known (^{4}), leads to the formation of aromatic β-ketoacetals; however, its first stage consists in exchange of halide for an alkoxy group, and since we followed its kinetics by the formation of halide ion, its subsequent course, leading to β-ketoacetals, was of no significance for our investigation. As aryl-β-chlorovinyl ketones we selected para-chlorophenyl ($R = n\text{-}ClC_6H_4$), para-bromophenyl ($R = n\text{-}BrC_6H_4$), and para-tolyl-β-chlorovinyl ketones ($R = n\text{-}CH_3C_6H_4$), which were prepared by the method described earlier (^{5}) and purified by vacuum distillation. Unfortunately, it was not possible to study the kinetics of the reaction for nitrophenyl-β-chlorovinyl ketone ($R = n\text{-}NO_2C_6H_4$), the only currently available β-chlorovinyl ketone containing a meta-orienting substituent, since the latter underwent changes in the course of the reaction (probably connected with reduction of the nitro group in alkaline medium) and did not give clear kinetics.

The kinetics of the chlorine-substitution reaction in aryl-β-chlorovinyl ketones was studied in the temperature range from −5 to −30°C. It was established that these are simple irreversible bimolecular reactions.

Method. The temperature was maintained constant to an accuracy of ±0.1° in an ultrathermostat filled with methyl alcohol. The alcohol was cooled in a refrigerating chamber with solid carbon dioxide. 1 ml of a 0.1 N ethereal solution of the ketone under study was diluted with absolute ethyl alcohol and cooled in the thermostat to the temperature of the experiment. Then a solution of sodium ethoxide in absolute alcohol, previously cooled to the same temperature, was added to it. The time of mixing of the cooled solutions, which were immediately thoroughly mixed, was taken as the start of the reaction.

were mixed. A series of experiments was set up, each of which was stopped after a definite interval of time. After completion of the experiment, the solution was diluted with water and acidified with nitric acid. The solution was washed with ether, and the ionic chlorine in the aqueous layer was determined by Volhard titration. The kinetic curves obtained are shown in Fig. 1. The rate constants, calculated on the basis of the kinetic measurements using the formula for an irreversible bimolecular reaction, are practically constant. The data obtained are collected in Table 1. For comparison, data from our work (3) concerning the kinetics of halide exchange in unsubstituted phenyl-β-chlorovinyl ketone are also added there.

(Figure: Fig. 1. Kinetic curves of the chlorine-substitution reaction in *p*-chloro-phenyl-β-chlorovinyl ketone (a) and in *p*-bromo-phenyl-β-chlorovinyl ketone (b))

Fig. 1. Kinetic curves of the chlorine-substitution reaction in *p*-chloro-phenyl-β-chlorovinyl ketone (a) and in *p*-bromo-phenyl-β-chlorovinyl ketone (b)

From the data presented it is evident that the activation energy of the reaction of substitution of the chlorine atom practically does not depend on the nature of the substituent in the aromatic nucleus. However, the pre-exponential factor in this case changes to a considerable extent–

Table 1

Temp., °C	$10^4/T$	*p*-$ClC_6H_4COCH=CHCl$		$C_6H_5COCH=CHCl$		$BrC_6H_4COCH=CHCl$		$CH_3C_6H_4COCH=CHCl$	
		$k \cdot 10^2$, min^{-1}	$lg(k \cdot 10^2)$	$k \cdot 10^2$, min^{-1}	$lg(k \cdot 10^2)$	$k \cdot 10^2$, min^{-1}	$lg(k \cdot 10^2)$	$k \cdot 10^2$, min^{-1}	$lg(k \cdot 10^2)$
–5	37.31	–	–	–	–	69.2	1.840	38.5	1.586
–10	38.02	144	2.158	115	2.060	47.2	1.674	28.0	1.447
–15	38.76	98	1.991	75	1.874	31.7	1.501	20.2	1.274
–20	39.52	64.2	1.807	49	1.690	21.1	1.324	11.8	1.072
–25	40.32	39.5	1.596	32.6	1.512	13.7	1.136	7.94	0.900
–30	41.15	26.3	1.420	21	1.322	–	–	–	–
E, kcal/mol			10.8		10.7		10.7		10.4
k_0			$24 \cdot 10^6$		$16 \cdot 10^6$		$6.5 \cdot 10^6$		$1.37 \cdot 10^6$

it increases in the direction of the series of substituents
$CH_3 < Br < H < Cl$. Naturally, in the same series the rate of the processes also increases at all the temperatures studied. Obviously, the influence of the substituent is manifested in a change in the activity of the carbonyl group, which determines the mobility of the halide in the β-position. The influence of the methyl group in tolyl-β-chlorovinyl ketone is quite regular, since its electron-donating character decreases the polarity of the carbonyl group and, consequently, the charge on the β-carbon atom reduces the mobility of the halide.

As regards the influence of a halogen atom in the para position of the phenyl ring in chloro- and bromophenyl-β-chlorovinyl ketones, it is, as is evident, different for the two aryl-β-chlorovinyl ketones mentioned: the para-chloro-substituted compound proves to be more reactive, whereas the para-bromo-substituted compound is less active than phenyl-β-chlorovinyl ketone. In all probability, this fact can be explained by the competing manifestation of the inductive and tautomeric effects of the halogen atom in the aromatic ring, acting in opposite directions:

$$\ddot{X}-\mathrm{C_6H_4}-\mathrm{C}(=\mathrm{O})\mathrm{CH{=}CHCl}\ :\ \ddot{X}-\mathrm{C_6H_4}-\mathrm{C}(=\mathrm{O})\mathrm{CH{=}CHCl}$$

In the case of parachlorophenyl-β-chlorovinyl ketone, the strong inductive effect of chlorine predominates, as a result of which the carbonyl group is additionally polarized and the mobility of the chlorine atom in the β-position increases. Conversely, for parabromophenyl-β-chlorovinyl ketone the inductive effect of the strongly polarizable bromine atom proves insufficient and is overridden by the oppositely directed tautomeric effect, which leads to a decrease in the activity of the chlorine atom in the β-position, which falls even below that in unsubstituted phenyl-β-chlorovinyl ketone.

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
27 VII 1962

REFERENCES

1. T. A. Kudryavtseva, N. M. Chirkov, *ZhFKh*, **32**, 2236 (1958).
2. T. A. Kudryavtseva, N. M. Chirkov, *ZhFKh*, **33**, 255 (1959).
3. T. A. Kudryavtseva, N. M. Chirkov, N. K. Kochetkov, *DAN*, **127**, No. 1, 108 (1959).
4. N. K. Kochetkov, E. Nifant' ev, S. D. Sokolov, *ZhOKh*, **29**, issue 9, 2570 (1959).

5. N. K. Kochetkov, A. Kh. Khorlin, M. L. Karpeiskii, *ZhOKh*, **26**, 595 (1956).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.