

LITERATURE CITED

1. V. M. Zhulin, T. V. Lipovich, and V. L. Antonovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2473 (1984).
2. Z. S. Kartasheva, A. B. Gagarina, and N. M. Émanuél', *Dokl. Akad. Nauk SSSR*, 212, 134 (1973).
3. V. M. Zhulin and M. G. Gonikberg, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 331 (1972).
4. A. T. Yasmenko, I. V. Khudyakov, A. P. Darmanjan, et al., *Chem. Scripta*, 18, No. 2, 49 (1981).
5. C. Eckert, *Ann. Rev. Phys. Chem.*, 23, 239 (1972).
6. V. M. Zhulin, *Rev. Phys. Chem. Jpn.*, 50, 217 (1980).
7. P. Marriott and D. Griller, *J. Am. Chem. Soc.*, 103, 1521 (1981).
8. C. Walling and G. Metzger, *J. Am. Chem. Soc.*, 81, 5365 (1959).

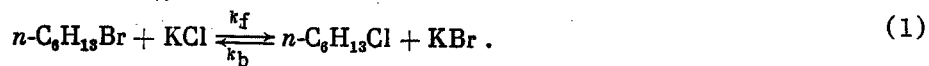
EXCHANGE REACTIONS IN TWO-PHASE CATALYTIC SYSTEMS.

3. KINETICS OF NUCLEOPHILIC SUBSTITUTION IN THE PRESENCE OF A SOLID IONOPHORE

I. A. Esikova and S. S. Yufit

UDC 541.127:542.97:542.944.3

Nucleophilic substitutions involving solid salts are widely employed in a number of syntheses [1-3]. No systematic study, however, has been made of the kinetics of such reactions. In this work a study was made of the kinetics of the replacement of the halogen in hexyl bromide RBr in the presence of solid KCl and a catalyst, tetrabutylammonium bromide Q^+Br^- in toluene



EXPERIMENTAL

Hexyl bromide having a T_b of 155.5°C was used. The content of the principal product, on the basis of GLC data, was not less than 90%; the remainder consisted of an inert admixture that did not participate in the reaction being investigated. The solid chemically-pure grade KCl was first dried at 150°C (1-5 mm), then crushed, and the 0.05-0.07-mm fraction was separated, and this fraction was again dried under vacuum. The Bu_4NBr was analytically pure grade; the T_b of the toluene was 118-119°C. The toluene was dried and distilled over Na; it was stored over molecular sieves.

The reaction was conducted in a thermostatted reactor fitted with a reflux condenser with a chlorocalcium tube and an efficient mixer. A rate of revolution of the mixer of 1900-2300 rev/min provided uniform mixing of the two phases; when the mixer was turned off, the system soon separated.

The method used for studying the kinetics was as follows: an amount of the solid salt, taken to provide a 5-7-fold excess relative to the RBr, was placed in the reactor, which had been heated to 84°C, and vigorously mixed for 40 min in order to activate it [4]; solid Q^+Br^- and 10 ml of toluene were added and mixed for an additional 10 min until the catalyst had completely dissolved. Then 15 ml of the hot RBr solution and the GLC standard, $C_{11}H_{24}$ in toluene, were poured into the reactor and the time count was begun. At predetermined time intervals the mixer was stopped, and after the layers had separated (30 sec), samples were taken from the organic layer by pipet through the reflux condenser. These were analyzed on the chromatograph under isothermal conditions at 100°C, using a glass column 2.4 × 0.005 m packed with N-AW DMCS (0.16-0.2 mm) impregnated with 5% SE-30. For measuring the concentrations, calibration constants were determined: RBr 1.8, RCl 1.53. The concentrations of

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 7, pp. 1520-1524, July, 1988. Original article submitted January 16, 1987.

TABLE 1. Calculation of the Equilibrium Concentration of Hexyl Chloride (C_e) and the Rate Constants by Different Methods ($[RCl] = 0.475$, $[QBr] = 0.04$ mole/liter, 13 g KCl, organic phase volume 25 ml, toluene, 84°C)

Method	C_e , mole/liter	K_e	k_f	k_b
			$\cdot 10^5 \text{ sec}^{-1}$	
From the equation for a first-order reversible reaction	0,367 (experimental)	3,4	7,7	2,3
By the K-S method	0,37 (calculated)	3,5	7,4	2,2
From the initial slope in semi-logarithmic coordinates			7,7	

TABLE 2. Effect of the Hexyl Bromide Concentration on the Kinetic Parameters of Reaction (1) (13 g KCl, organic phase volume 25 ml, $[QBr] = 0.04$ mole/liter, toluene, 84°C)

$[RBr]_0$, mole/liter	K_e	k_f	k_b	$k_f \cdot [RBr]_0 \cdot 10^5$, mole/(liter · sec)
		$\cdot 10^{-5} \text{ sec}^{-1}$		
0,475	3,5	7,4	2,2	3,5
0,7	3,4	7,4	2,2	5,2
1,0	2,85	6,67	2,35	6,67
1,25	2,68	5,39	2,01	6,74
1,71	2,66	4,07	1,53	6,96
2,0	2,64	3,92	1,48	7,84
2,4	2,7	3,28	1,22	7,87

TABLE 3. Effect of the Concentration of Bu_4NBr on the Kinetic Parameters of Reaction (1) (13 g KCl, organic phase volume 25 ml, $[RBr] = 0.9-1$ mole/liter, toluene, 84°C)

$[Bu_4NBr]$			K_e	k_f	k_b
g	mmole	mole/liter		$\cdot 10^5 \text{ sec}^{-1}$	
0,08	0,25	0,01	3,5	2,2	0,62
0,16	0,5	0,02	2,7	4,0	1,47
0,23	0,7	0,029	3,4	5,4	1,6
0,32	1,0	0,04	2,6	7,0	2,7
0,64	2,0	0,08	3,3	9,3	2,8

TABLE 4. Effect of Additions of KCl and KBr on the Rate Constants and Equilibrium Constant of Reaction (1) (solid salt 0.086 mole, $[Bu_4NBr] = 0.04$ mole/liter, organic phase volume 12.5 ml, $[RBr] = 1.0$ mole/liter, toluene, 84°C)

No.	KCl	KBr	K_e	k_f	k_b
	mole			$\cdot 10^5 \text{ sec}^{-1}$	
1	0,086	0	2,6	7,0	2,7
2	0,086	0,0092	3,2	4,7	1,48
3	0,086	0,0172	2,85	3,62	1,27
4	0,086	0,043	2,85	3,96	1,39
5	0	0,086	2,75	5,5	2,0
6	0,0092	0,086	2,92	4,68	1,6
7	0,0172	0,086	2,75	3,77	1,37
8	0,043	0,086	2,91	3,97	1,36

the $C_6H_{11}Br$ and the $C_6H_{11}Cl$ in the liquid phase were determined to within $\pm 5\%$. The amount of $C_6H_{13}Br$ lost in the course of the experiment was equal to the amount of $C_6H_{13}Cl$ that accumulated. No other products were detected under the standard conditions. The scatter in the data points when identical experiments were made averaged $\pm 7-8.5\%$; in the region of low hexyl chloride concentrations, deviations from the mean concentration at times reached $\pm 20\%$.

The reaction was carried out under conditions of a pseudo-first-order reaction in RBr. The kinetic data on the consumption of RBr do not follow the laws for an irreversible first-order reaction, the points in the final sector of the curve deviating upward from the initial slope of the straight line. The kinetic curves for RBr and RCl are linearized in coordinates for a reversible first-order reaction. The time required to reach equilibrium is usually lengthy, so that the K-S method was used for the calculations [5]. Comparing the values of the equilibrium constants and the rates of the forward and reverse reactions K_e , k_f , k_b calculated from the equation for a reversible first-order reaction with the values calculated by Kezdy-Swinbourne method, we see the suitability of the latter for the calculation (Table 1). The Kezdy-Swinbourne method provides the following precision in calculating one kinetic curve: for the equilibrium concentration of RCl $C_e \pm 1.5\%$, $K_e \pm 6$, $k_f + k_b \pm 2.5$, $k_f \pm 2.7$, for $k_b \pm 7\%$. The scatter in the values of the constants calculated for identical runs may be greater, and are $K_e \pm 13$, $k_f \pm 20$, $k_b \pm 25\%$. For this reason, for the analysis below we have used an average value of the constants obtained from those runs for which the deviation in the values of the calculated constants was no more than $\pm 8.5\%$.

The order of the reactions in the reactants was determined at $84^\circ C$ in toluene (Tables 2 and 3). Additions of the salts KCl or KBr to the starting mixture slows the replacement (Table 4), while additions of RCl (for a slight variation in [RBr]) have practically no effect on the K_e , k_f , and k_b constants (Table 5).

RESULTS AND DISCUSSION

The cessation of a reaction in a system consisting of a solid salt and an organic phase may be due to a thermodynamic reaction or to processes characteristic of two-phase catalytic systems: inhibition by a lipophilic anion (binding of the catalyst) [6], the breakdown of the catalyst QX, the saturation of the reaction sites of the salt during the adsorption of the reactants, etc. In order to establish the true reason for the cessation of the replacement reaction a number of special runs were made, in the course of which it was established that for reaction (1), thermodynamic equilibrium is established (cf. Tables 2-5). That the reaction is reversible is supported by the fact that adding RCl to the starting mixture reduces the rate of consumption of RBr, the reduction being the stronger, the greater its initial concentration (Fig. 1), while the rate constants for replacement remain almost unchanged (Table 5). The value of K_e does not change when the amount of catalyst and substrate are varied. The reverse reaction, the conversion of RCl to RBr in the presence of KBr and Bu_4NBr under the same conditions as for the forward reaction, produces essentially the same equilibrium mixture and is characterized by a similar value of K_e , as calculated by the Kezdy-Swinbourne method (Table 4, Nos. 1 and 5). This suggests that equilibrium exists at all stages of the process.

The variable order in the catalyst (Table 3), the reduction of the reaction order in RBr to less than first at concentrations less than 0.7 mole/liter (Table 2), and exceeding the specific rate of replacement with increasing amounts of KCl [4] differ from the kinetic rules of replacement in the system consisting of aqueous and organic phases [8]. Furthermore, in the presence of a solid ionophore, ion exchange does not occur between the QBr catalyst and KCl [7]. This rules out the possibility of nucleophilic substitution occurring via the two-step scheme in (A) proposed earlier by Starks



for the water/organic-phase system [8, 9]. The necessity therefore arises of seeking new schemes in agreement with the experimental data obtained in the presence of a solid ionophore.

The results of our investigation suggest that the nature of the change in the rate constant of the forward reaction when the concentration of the substrate increases is related to its reverse reaction with QBr or the solid KCl



TABLE 5. Effect of the Concentration of Hexyl Chloride on the Rate Constants and the Equilibrium Constants of Reaction (1) (13 g KCl, organic phase volume 25 ml, $[Bu_4NBr]$ 0.04 mole/liter, toluene, 84°C)

[RCl]	[RBr]	$[\bar{X}]^*$	K_e^{**}	k_f	k_b
mole/liter				$\cdot 10^5 \text{ sec}^{-1}$	
—	1,0	0,72	2,6	7,0	2,7
0,18	0,95	0,69	3,35	6,7	2,0
0,2	0,84	0,6	3,4	7,9	2,34
0,35	0,92	0,63	3,3	8,9	2,7

* $[\bar{X}] = [RBr]_0 - [RBr]_e$, where $[RBr]_e$ is the equilibrium concentration of RBr.

** $K_e = k_f/k_b = ([RCl]_0 + [\bar{X}])/([RBr]_0 - [\bar{X}])$.

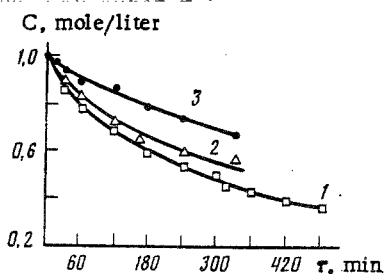
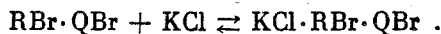


Fig. 1. Change in the rate of reaction (1) with the addition of hexyl chloride to the starting mixture: 1) without additions; 2) 0.182; 3) 0.34 mole/liter.

Rearrangement within the $RBr \cdot KCl$ complex could produce RCl , but this does not occur, since the replacement does not occur without QBr . This is in agreement with the idea [10] that the leaving group must be solvated. Halide exchange is not possible in the formation of the $RBr \cdot QBr$ complex, but activation of the alkyl halide occurs, facilitating its interaction with the solid ionophore



Earlier we showed [4] that after preliminary activation, solid KCl exhibits clearly nucleophilic properties due to the formation of "nonequilibrium" Cl^- ions. The exceeding of k_f observed at $KCl/RBr \geq 7$ [4] was caused by adsorption of QBr or $RBr \cdot QBr$ onto activated sites of the ionophore. This is also indicated by the variable order in Bu_4NBr . One can apparently regard reaction (1) as occurring according to a mechanism including a reversible step involving three components, the substrate, the ionophore, and a catalyst, that forms binary complexes and one ternary complex, the ternary complex being attached to the surface of the solid salt.

A characteristic feature of the process, associated with the use of a solid ionophore, is the inhibiting of the replacement by one of the products of the reaction. The introduction of additions of the product salt (Table 4) into the starting mixture does not affect K_e or the equilibrium concentrations of RCl and RBr , but k_f and k_b decrease. If the starting salt: product salt mole ratio is less than or equal to 5, further additions of the product salt have little effect on the rate of replacement. It is interesting to note that when another product of reaction (1), RCl , is added, no significant changes in k_f and k_b were observed (Table 5). The inhibiting action of the product salt may be due to the coverage of the reaction sites of the KCl . Such an explanation appears unconvincing, however, since the reaction proceeds when the solid salt has been finely ground, ensuring that a "steady-state" concentration of Cl^- active sites is maintained. Another reason for the inhibiting effect of the product salt may be the formation of a nonproductive ternary $KBr \cdot RBr \cdot QBr$ complex by adsorption of $RBr \cdot QBr$ on KBr or of $RCl \cdot QCl$ on KCl , respectively, which would lead to a decrease in the concentration of the substrate and catalyst in the organic phase. Taken all together, the data indicate that the process proceeds on the surface of the solid salt via the formation of a ternary complex. We shall provide a more detailed mechanism for this reaction in a later communication.

CONCLUSIONS

1. The nucleophilic substitution of bromine by chlorine in hexyl bromide in the presence of a solid ionophore and tetrabutylammonium bromide in toluene follows the rules for a reversible reaction of the first order in the substrate.
2. The dependence of the rate constants of the forward and the reverse reactions on the concentrations of hexylbromide and of tetrabutylammonium bromide has been studied. The reaction is first order in all components at low concentrations, and less than unity at higher concentrations.
3. One of the reaction products, the solid salt, inhibits the replacement, reducing the rate of both the forward and the reverse reactions.
4. A reaction scheme is proposed whereby the process occurs on the surface of the solid ionophore via a ternary complex, the breakdown of which produces the reaction products.

LITERATURE CITED

1. J. Ugelstad, T. Ellingsen, and A. Berge, *Acta Chem. Scand.*, 20, 1593 (1966).
2. C. L. Liotta, E. L. Grisdale, and H. P. Hopkins, *Tetrahedron Lett.*, 4205 (1975).
3. A. Jonczyk, M. Ludwikow, and M. Makosza, *Angew. Chem. Int. Ed.*, 17, 62 (1978).
4. O. I. Danilova, I. A. Esikova, and S. S. Yufit, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2422 (1986).
5. A. J. Cornish-Bowden, *Principles of Fermentation Kinetics* [Russian translation], Mir, Moscow (1979), p. 22.
6. A. Brändström and H. Kolind-Andersen, *Acta Chem. Scand.*, 29, 201 (1975).
7. O. I. Danilova, I. A. Esikova, and S. S. Yufit, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 309 (1988).
8. C. M. Starks and R. M. Owens, *J. Am. Chem. Soc.*, 95, 3613 (1973).
9. C. M. Starks, *J. Am. Chem. Soc.*, 93, 1951 (1971).
10. C. G. Swain and C. B. Scott, *J. Am. Chem. Soc.*, 75, 141 (1953).

PREPARATION AND REACTIVITY OF METAL-CONTAINING MONOMERS.

7. SYNTHESIS AND STUDY OF TRANSITION METAL ACRYLATES

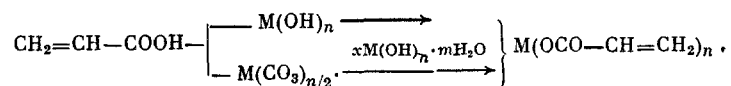
G. I. Dzhardimalieva, A. D. Pomogailo,
V. I. Ponomarev, L. O. Atovmyan,
Yu. M. Shul'ga, and A. G. Starikov

UDC 541.42:542.91:548.737:547.357

Metal-containing monomers (MCM) based on unsaturated acid salts are the most common group of comparatively well polymerizable MCM. The data on the composition and structure of this class of MCM are limited and isolated, although individual members of these MCM have been known for a comparatively long time. Since the reactivity of such compounds is determined by the nature of the transition metal, a comparative analysis of the structure and properties of the acrylates in a series of transition metals was of interest.

DISCUSSION

Synthesis of Transition Metal Acrylates. The reaction of transition metal (hydro)oxides or their basic carbonates with unsaturated acids is an effective method of synthesis of MCM of this class [1, 2]



For optimizing the conditions of synthesis, the effect of the ratios of the starting components, reaction temperature, and synthesis time were determined. Of the different methods of con-

Branch of the Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 7, pp. 1525-1530, July, 1988. Original article submitted January 16, 1987.