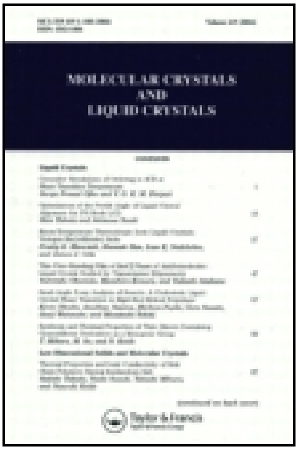

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THE MECHANISM OF OLEFIN HALOGENATION AND HYDROHALOGENATION IN THE SOLID PHASE

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Abstract This report deals with IR-investigation of solid state halogen and hydrohalogen addition to olefins at 75-150K. Molecular complexes are formed under codeposition of the reagent vapour on a cooled surface. Complexation degree is determined by kinetic and thermodynamic factors. The kinetic law depends on the sample composition, complex stability and matrix rigidity. Complexes, including two acceptor molecules, are most reactive. The results can be explained on the basis of molecular mechanisms of addition.

INTRODUCTION

So far addition of halogens and hydrohalogens to multiple bonds remains one of few processes that are known to go quantitatively at the boiling temperature of liquid nitrogen without external initiation. Halogenation is most suitable to study the kinetics of solid-state reactions since it enables us to determine kinetic characteristics in the systems unpertubed by external initiation. Halogenation proceeds easily at low temperature where its peculiarities are most markedly manifested. In the present work we report the results of quantitative investigations into kinetics of low-temperature solid-state halogenation and hydrohalogenation of olefins.

RESULTS AND DISCUSSION

The optimal technique for preparation of samples for IR-investigation are the codeposition of reagents on a cold surface (75-80K) in the molecular beam mode.
The degree of reagent complexation in the solid state de-

pends on the support temperature, reagent ratio and codeposition rate. This is illustrated by the spectra of solid state co-condensates of hydrogen chloride and 2-methylbutene-2 with slight excess of HCl (10-30%). The samples were almost identical in composition but were produced with different condensation rates, V_c. At small (10^{15}molecules/cm^{2}s) and large (10^{17}molecules/cm^{2}s) V_c values the sample contains a considerable amount of uncomplexed olefin (absorption band 1680 /cm) and hydrogen chloride. In the spectrum of the sample produced at the intermediate condensation rate, only the bands of olefin in complexes of 1:1 (at 1660 /cm) and 2:1 (at 1650 /cm) composition are visible. The degree of complexation amounts to 100%. The portion of the complex of 2:1 composition increases with decreasing condensation rate. Such dependence demonstrates that, unlike the liquid phase reactions, the amount of complex in the solid-state samples is determined not only by thermodynamic but also by kinetic factors.

To prove that the solid-state reaction proceeds via direct transformation of molecular complexes rather than by the interaction of uncomplexed molecules, the degree of complexation was controlled by selecting the condensation regime. The straight-forward correlation between reactivity and the complexation degree is evident from Table 1.

TABLE 1 The dependence of reaction rate in the system 2-methylbutene-2 - HCl on the degree of complexation (HCl: olefin = 6:1, 80K)

Degree of complexation, %	Reaction rate during condensation % conversion/hour	Reaction rate during thermal treatment % conversion/hour
100	39	25
50	22	13
0	0	0

Another important factor for the solid-state reaction is composition of the complex. The degree of olefin transformation in a 7-fold excess of HCl under 100% complexation is presented in Table 2 as a function of 1:1 and 2:1 complex ratio. The reactivity of the system is determined by the amount of the complex of 2:1 composition. Similar experiments for other systems revealed the general rule: the most reactive complexes are those where a molecule of olefin is complexed with a greater number molecules. In other words, complexes with the greatest degree of double bond perturbation are the most reactive.

TABLE 2 The dependence of the rate 2-methylbutene-2-hydrochlorination on the ratio of complexes of 2:1 and 1:1 composition at 80K

Ratio of the band intensities of the 2:1 to 1:1 complexes	1	0,9	0,8	0,7	0,6	0,4
reaction rate during condensation, % conversion/hour	41	30	22	20	15	6
reaction rate during thermal treatment, % conversion/hour	27	25	18	13	10	4

The solid-state hydrohalogenation is characterised by an interesting peculiarity that can not in principle be observed in solution or the gas phase. The primary reaction product is not the corresponding alkylhalide, but its complex with hydrohalogen. The IR bands of the solid-state hydrohalogenation products do not match the bands for the individual solid alkylhalides but fully coincide with the bands of their complexes with the corresponding hydrohalogens. It would thus be possible to represent the scheme of the reaction as a transformation of one molecular complex into another:

$$OL \cdot 2HX \longrightarrow P \cdot HX$$

where OL is olefin, P is alkylhalide, X, chlorine or bromine atom. This result was substantiated by quantum-mechanical calculations for the hydrogen fluoride - ethylene system (see reference 1).

Formation of such a complex causes the increase in thermal effects of the reaction by complexation enthalpy - by 3-4 k cal/mole - as compared to bimolecular reactions in the gaseous phase. From the point of view of correlation and in the context of similar reaction rates and thermal effects, this can be considered as one of the reasons for the high reactivity of complexes between olefins and halogens or hydrohalogens in the condensed phase.

The experimental data obtained so far are best interpreted in terms of a molecular mechanism with a six-membered transition state. The molecular mechanism was thoroughly analysed in reference 2. Here we will only touch upon additional reasons in favour of this mechanism in terms of solid-state systems. It is a fact that the reaction proceeds at a low temperature, for example, at the boiling point of liquid nitrogen. This is an indication of an extremely low activation energy. Such activation energy is typical for rearrangements of bonds in cyclic systems with participation of halogens (ref. 2,3). Conversely, the dissociation into ions or radicals in the absence of an effective solvation requires high energy losses. Therefore the ionic and radical mechanisms under conditions of solid-state addition are most unlikely. On the other hand, the molecular mechanism agrees with the absence of strong influence of the matrix polarity on the rate of solid-state processes. Thus, a similar rate is observed for chlorination of olefin in a 6-fold excess of polar dichloroethane and non-polar difluorodichloromethane. The molecular mechanism is also substantiated by stereochemistry. It was demonstrated in ref.2 that two possible six-membered transition states result in either cis- or trans-addition. Accordingly, both types of products are formed in solid-state halogenation and hydrohalogenation of olefins. The product ratio depends on olefin structure: trans-addition is more typical for cyclohexene and related compounds, cis-addition - for alkenes. The solid-phase hydrobromination of phenylacetylene also gives cis-adduct.

Solid-state chlorination of ethylene, unlike other processes, proceeds via a complex of equimolecular composition. Interaction with a free chlorine molecule increases the chlorination rate but is in no way necessary. The two alternative pathways are the cyclic rearrangement of the complex or the intermediate formation of ionic pair.

In the first case cis-addition should proceed with the formation of gauche-1,2-dichloroethane. In the case of the ionic mechanism, the bridged structure of the chloronium cation should result in trans-addition. Setting the equilibrium too rapidly between conformers of 1,2-dichloroethane makes these pathways indistinguishable in solution. However in the solid state at 80-90 k such equilibrium is not yet reached and the prevailing stereochemistry of addition can be determined. The kinetic curves for the solid-state chlorination of ethylene are plotted in Fig.1. Their shape is typical of consecutive reactions, with gauche-1,2-dichloroethane being an intermediate product. Its rearrangement into trans-conformer is apparently caused by partial utilization of heat from the exotermic reaction. In a CCl_4 or CF_2Cl_2 matrix the isomerization can be prevented and gauche-1,2-dichloroethane will be the main reaction product.

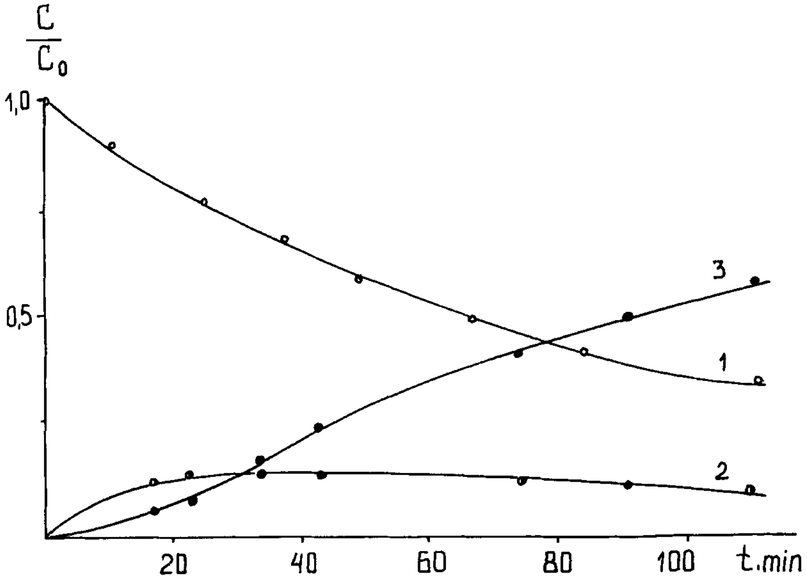

FIGURE 1. Kinetic curves for the consumption of ethylene-chlorine 1:1 complex (1) and formation of gauche-(2) and trans-(3)-1,2-dichloroethane at 100K. $Cl_2/C_2H_4 = 2,7$.

The results are in good agreement with a four-membered cyclic transition state. The transformation of molecular complexes occurs in liquid and solid phases. Apparently, the nature of the transition states in both phases is also similar. The differences are manifested in the kinetics of halogenation and hydrohalogenation.

If the solid state process developed identically with the liquid phase reaction, its kinetics would correspond to the first order equation for the reactive complex. In fact, such kinetics (we call it "standard" or "normal") is observed in all systems in question under certain conditions. In the general case solid state kinetics can be divided into "standard", "retarded" and "step-wise" (see ref.4 and 5). A detailed kinetic study of solid state halogenation and hydrohalogenation revealed that, by varying conditions, all three types of kinetic law can be observed in each of the systems in question. The total kinetic data suggest the dependence of the kinetic law on the number of particle types in the reaction system. For instance, the following scheme can be proposed for ethylene chlorination:

particles in the system	complexes of reagents	complexes+excess of one reagent or diluent	complexes+ excess of one reagent+excess of diluent
type of kinetics	standard	retarded	step-wise
linearity coordinates	$\ln(C/C_o)$ vs t	$\ln(C/C_o)$ vs t^a	(C/C_o) vs $\ln(t)$

The kinetic data for solid-state halogenation are best interpreted in terms of a polychronic reaction model where the step-wise and retarded kinetics are explained by the rate constant distribution (ref. 4,6). The step-wise kinetics correspond to a wide, and retarded kinetics - to a relatively narrow distribution.

The distribution of complexes by their reactivity, in our opinion, is either caused by different mutual orientation of molecules in complexes or different interaction of complexes with the surrounding molecules.

The most chemically homogeneous samples consist only of complexes. In this case the environment of all reactive particles is almost identical. The differences in orientation inside complexes are also not pronounced due to the mutual association of complexes. The existence of such association with the energy of 2-5 kJ/mole was collaborated by spectral data (see ref.7).

The mutual ordering effect of complexes results in the additional levelling in terms of reactivity. In that case standard kinetics would be most probable.

A large excess of one of the reagents or diluent will slacken the association. In mutually unbonded complexes the probability of different orientations of donor and acceptor molecules increases. Complexes become kinetically non-equivalent and transition to retarded kinetics is observed.

In the least homogeneous samples with an excess of both a reagent and a diluent, the distribution can be caused by three reasons: varying molecular orientation in complexes, their chemical environment, difference in chemical composition, different probability of forming the reactive pair complex of 1:1 composition + halogen or hydrohalogen molecule. Here the distribution is the widest and, consequently, the kinetics is step-wise. Some obtained minimum and maximum rate constants for consumption ethylene-chlorine complexes at various sample composition are given in Table 3.

TABLE 3 Kinetics parameters of solid-state addition to olefin

System	ratio Cl_2 or HX to olefin	E, kJ/mole	T,K	rate constants	
				max. ($x10^4$, s^{-1})	min. s^{-1}
C_2H_4-Cl_2 in CF_2Cl_2	6	-	97	190	$3\cdot10^{-17}$
C_2H_4-Cl_2	50	-	97	8.5	10^{-5}
C_2H_4-Cl_2	6	-	97	8.5	$8\cdot10^{-6}$
C_2H_4-Cl_2	2,7	24	97	0.4#	-
c-C_6H_{10}-Cl_2	0,5	13	94	0.7#	-
c-C_6H_{10}-Cl_2 in CO_2	2	8	94	0.5#	-
C_5H_{10}-HCl	5	12	92	2.9#	-
C_5H_{10}-HBr	0,3	8	105	0.5#	-

Note: # - normal first order constants

Thus, the kinetic parameters of solid-state halogenation and hydrohalogenation are a complex function of the composition of systems and experimental conditions. The measured, under conditions of the standard kinetics, first order rate constants and activation energies are similar to those obtained in corresponding systems in solution in non-polar media. With the exception of ethylene chlorination, activavation energies are lower or close to energies necessary

to break the intermolecular bonds in donor-acceptor complexes of reagents. This fact can serve as additional evidence for the assumption that the addition products are formed immediately from molecular complexes without their dissociation into reagent molecules or ions.
On the whole, the obtained data show that solid-state halogenation and hydrohalogenation yields additional information on the mechanism of this classical organic chemical process, its intermediate stages and primary products. There is every reason to believe that the effort one has to make in studying the low-temperature solid-state reactions is worth all the trouble.

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