

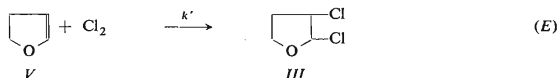
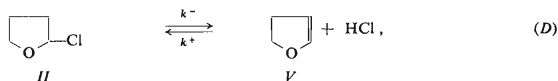
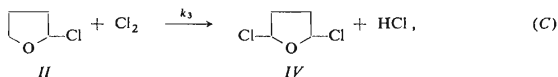
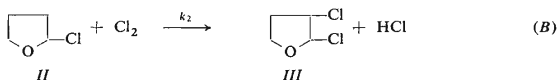
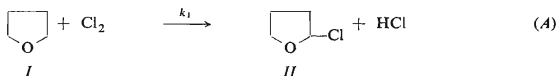
ACTIVATION ENERGIES OF THE CHLORINATION OF TETRAHYDROFURAN

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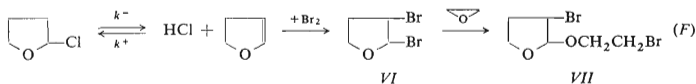
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When subjected to photochlorination at room temperature, tetrahydrofuran (*I*) yields 2,3-dichlorotetrahydrofuran (*III*) as the main product. This compound is relatively stable and was considered to be^{1,2} the first product of the chlorination of compound *I*. At lower temperature (around -25°C) and under otherwise identical experimental conditions 2-chlorotetrahydrofuran (*II*) becomes the principal product of the chlorination. Further chlorination gives 2,5-dichlorotetrahydrofuran^{3,4} (*IV*). Compound *II* is not thermally stable, it can be stored at -15°C for a limited period of time, without decomposition only at the temperature of dry ice. These facts compelled us to verify a proposed mechanism of the chlorination of compound *I* (ref.⁴) in which the already known rules for chlorination of acyclic ethers were taken into account. We deal



here with a system of radical substitution reactions. Equation (*B*) represents the result of the two processes described by equation (*D*) and (*E*). Reactions (*B*) and (*C*) are competitive. As chlorine (or chlorine radical, since the equations are the simplified description of radical chain photochlorination) is present in all the three equations, the system consisting of equation (*A*) and the sum of equations (*B*) and (*C*) can be considered as consecutive competitive process

from the point of view of kinetic analysis and mathematical treatment. Therefore it is not necessary to solve the problem of the influence of chlorine concentration and photoinitiation⁵. As we had not succeeded in detecting 2,3-dihydrofuran (*V*) as an intermediate product of the process described in equation (*B*), the course of the reaction (*B*) was verified by the following experiment:



The reaction was led to 2-(2-bromoethoxy)-3-bromotetrahydrofuran (*VII*) since we had not been able to isolate 2,3-dibromotetrahydrofuran (*VI*) in sufficient purity.

A mathematical description of the system of reactions (*A*)–(*C*) is represented by a set of differential equations (*I*)–(*4*), the solution of which yields equations (*5*)–(*8*). The symbols in brackets denote the reactants (see text). The subscript zero denotes the initial concentration of the corresponding compound.

$$-d[\text{I}]/dt = k_1[\text{I}] \quad (1)$$

$$d[\text{II}]/dt = k_1[\text{I}] - k_B[\text{II}] \quad (2)$$

$$d[\text{III}]/dt = k_2[\text{II}] \quad (3)$$

$$d[\text{IV}]/dt = k_3[\text{II}] \quad (4)$$

$$[\text{I}] = [\text{I}]_0 \exp(-k_1 t) \quad (5)$$

$$[\text{II}] = k_1/(k_B - k_1) [\text{I}]_0 [\exp(-k_1 t) - \exp(-k_B t)] \quad (6)$$

$$[\text{III}] = \frac{k_1 k_2}{k_B - k_1} [\text{I}]_0 \left[\frac{1 - \exp(-k_1 t)}{k_1} - \frac{1 - \exp(-k_B t)}{k_B} \right] \quad (7)$$

$$[\text{IV}] = \frac{k_1 k_3}{k_B - k_1} [\text{I}]_0 \left[\frac{1 - \exp(-k_1 t)}{k_1} - \frac{1 - \exp(-k_B t)}{k_B} \right] \quad (8)$$

$$k_B = k_2 + k_3 \quad (9)$$

By analysis of the dependence of concentration of the intermediate *II* on the concentration of compound *I*, i.e. by dividing Eq. (2) by (1), one obtains Eq. (10), the solution of which for $q \neq 1$ Eq. (11).

$$-d[\text{II}]/d[\text{I}] = 1 - k_B[\text{II}]/k_1[\text{I}] \quad (10)$$

$$[\text{II}]/[\text{I}]_0 = \frac{q}{q-1} \left(\frac{[\text{I}]}{[\text{I}]_0} \right)^{1/q} - \frac{q}{q-1} \frac{[\text{I}]}{[\text{I}]_0} \quad (11)$$

$$q = k_1/k_B \quad (12)$$

TABLE I

Maximum Conversions of Compound *I* to Compound *II* and the Calculated Values of Rate Constants k_1 , k_2 , k_3 and k_B

$^{\circ}\text{C}$	t_{max} , min	$[\text{II}]/[\text{I}]_{0\text{max}}$	q	$[\text{Cl}_2]$, mmol/l
-25	80 ± 5	0.625 ± 0.107	4.800 ± 1.600	55.0
-10	70 ± 5	0.462 ± 0.056	2.210 ± 0.990	17.5
5	60 ± 5	0.400 ± 0.036	1.020 ± 0.200	10.0
20	55 ± 5	0.326 ± 0.007	0.780 ± 0.030	8.0
40	50 ± 5	0.127 ± 0.003	0.193 ± 0.008	5.5

Function (*II*) passes through a maximum with coordinates $[\text{II}]/[\text{I}]_{0\text{max}}$ and $[\text{I}]/[\text{I}]_{0\text{max}}$ expressed by Eqs (13) and (14), respectively.

$$[\text{II}]/[\text{I}]_{0\text{max}} = q^{1/(1-q)} \quad (13)$$

$$[\text{I}]/[\text{I}]_{0\text{max}} = q^{q/(1-q)} \quad (14)$$

By combining Eqs (5) and (14) one obtains Eq. (15) from which the constant k_1 can be calculated as a function of the time t_{max} needed for attaining the maximum concentration of product *II*.

$$k_1 = \frac{2.3q}{(q-1)t_{\text{max}}} \log q \quad (15)$$

Determination of maximum content of compound *II* and the time t_{max} , with the aid of Eqs (13) and (15), enables us to obtain the values of constants q and k_1 and hence to solve Eq. (12) for k_B , the sum of the rate constants of competitive reactions (*B*) and (*C*). A relative change in concentrations of products of these reactions is described by Eq. (16), whose solution (17) determines the dependence of the rate constants on the concentration of products.

$$d[\text{III}]/d[\text{IV}] = k_2/k_3 \quad (16)$$

$$[\text{III}]/[\text{IV}] = k_2/k_3 \quad (17)$$

The constants k_2 and k_3 can be thus obtained from the ratio of the concentrations of products (*III*) and (*IV*) and the value of k_B .

Experimental results were analysed by means of Eq. (11). The values of the maximum content of reaction intermediate *II*, t_{max} and chlorine concentration are given in Table I, along with the theoretical values calculated for different temperatures. A good agreement between theoretical and experimental results is demonstrated in Fig. 1. Compound *IV* is present in detectable amounts only when chlorination is carried out at -10 and -25°C . The ratio of concentration of both dichlorotetrahydrofuran isomers formed $[\text{III}]/[\text{IV}]$ was found to be 3.53 ± 1.39 at -10°C and 0.516 ± 0.088 at -25°C . With the aid of a modified Arrhenius equation and the above data

TABLE I
(Continued)

$k_1 \cdot 10^2$ min^{-1}	$k_B \cdot 10^2$ min^{-1}	$k_2 \cdot 10^2$ min^{-1}	$k_3 \cdot 10^2$ min^{-1}
2.443 ± 0.318	0.573 ± 0.191	0.194 ± 0.065	0.379 ± 0.126
2.008 ± 0.423	1.137 ± 0.509	0.860 ± 0.385	0.277 ± 0.124
1.685 ± 0.170	1.718 ± 0.337	—	—
1.613 ± 0.148	2.071 ± 0.190	—	—
0.794 ± 0.080	4.121 ± 0.415	—	—

it was found that the difference of the activation energies of the formation of these derivatives ΔE amounts to 16.10 ± 3.62 kcal/mol. This value agrees well with the difference of the activation energies determined for single processes.

The values of constants k_1 and k_3 (Table I) are apparently indicative of a negative activation energy of the formation of compounds *II* and *IV*. These values include, however, the concentration of chlorine, which increases with increasing temperature, and also reflect the effect of photo-initiation. From k_1 and k_3 for -10 and -25°C , after correction for chlorine concentration, the following activation energies for the reactions (A)–(C) were obtained: $E_1 = 8.12 \pm 1.86$ kcal/mol, $E_2 = 24.92 \pm 5.33$ kcal/mol, and $E_3 = 9.41 \pm 3.27$ kcal/mol. Photoinitiation has not been studied in detail.

EXPERIMENTAL

Compounds used. Tetrahydrofuran was dried with metallic sodium, freed from peroxides by boiling it with solid potassium permanganate and freshly distilled prior to its application. Electrolytic chlorine from pressure cylinder was purified by concentrated sulphuric acid, as was

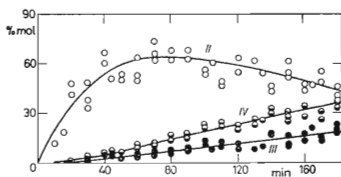


FIG. 1

Concentration Dependence of 2-Chlorotetrahydrofuran (*II*), 2,3-Dichlorotetrahydrofuran (*III*), and 2,5-Dichlorotetrahydrofuran (*IV*) on Chlorination Time of Tetrahydrofuran at -25°C

also prepurified nitrogen. Ethanol, chlorobenzene and toluene were dried in the usual manner and then rectified. The purity of the liquids was checked by gas chromatography.

Chlorination was carried out in a glass cylindrical vessel immersed into a temperature-controlled water (for temperatures above 0°C) or ethanol (for lower temperatures) bath provided with a stirrer and an automatic control system with a contact thermometer and an electric heater. Dry ice was used as the coolant. It was charged into open ampules containing ethanol, which were inserted into the bath. By this way the temperature was controlled within 1°C. The chlorination vessel was provided with a double-wall quartz tube with evacuated space between the walls. The tube was located in the axis of the vessel and tightly sealed with a stopper. A 100 W mercury lamp was placed into the tube. Chlorine was charged by a constant rate in a stream of nitrogen and led to the bottom of the vessel to ensure stirring up the contents. The gases (nitrogen and excess of hydrogen chloride) were drawn off via a reflux condenser cooled with dry ice. The chlorination vessel was equipped with a control thermometer and a sampling assembly consisting of a capillary tube of 1 mm diameter, leading to the bottom of the vessel and topped with a calibrated vessel and connection to vacuum for pumping in the medium.

From the calibrated vessel, the samples were then taken off by means of a stopcock.

Analysis. The samples were transferred to a flask containing anhydrous ethanol. The complete alcoholysis of a chloroether and the removal of hydrogen chloride were effected by adding anhydrous sodium carbonate to neutral reaction. After sodium chloride and excess sodium carbonate set down, the liquid phase was analysed on a Chrom II gas chromatograph equipped with a flame-ionization detector (a column filled with 10% poly(ethylene glycol adipate) on Rysorb BLK, 60 and 120°C oven temperature). Chlorobenzene (added to a chlorination mixture) and toluene (added to the alcohol) were used as internal standards. The composition of the chlorination mixture: tetrahydrofuran 45 ml (0.555 mol, conc. 11.1 mol/l), chlorobenzene 5 ml (0.049 mol, conc. 0.98 mol/l). The volume of the sample assembly was 1.43 ml. The composition of the alcohol for sampling: 97.9% v. of ethanol and 2.1% v. of toluene. Seven milliliters of this mixture was used for the analysis of each sample. The rate of chlorine inlet was 180 ml per min. Its concentration was determined by measuring absorption of the light of the mercury lamp at 3650 Å at all the temperatures used. The absorption was measured by means of a photocell and a galvanometer and taken as the measure of the chlorine concentration, which was (in CCl_4), after calibration, determined by iodometric titration on the excess of sodium thiosulphate.

Preparation of 2-(2-bromethoxy)-3-bromotetrahydrofuran (VII). Compound *II* was prepared⁴ by chlorination of substance *I*. Then bromine was added dropwise to a solution of the chloroether *II* in ether at 4°C. The reaction mixture was then bubbled with nitrogen which was led to an ethereal solution of pyridine; the pyridinium hydrochloride formed had m.p. 82°C. The reaction mixture was then freed from the hydrogen chloride and allowed to react with ethylene oxide. Distillation under reduced pressure afforded 72% yield of the main fraction boiling 131–133°C/15 Torr, n_D^{20} 1.5145, d_4^{20} 1.7876, M_R calculated: 46.52, found: 46.34. For $\text{C}_6\text{H}_{10}\text{Br}_2\text{O}_2$ (273.9) calculated: 26.30% C, 3.68% H, 58.37% Br; found: 26.50% C, 3.74% H, 57.10% Br.

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