

**INVESTIGATION OF THE EXCHANGE REACTIONS OF c-ALKYL  
IODIDES OF DIFFERENT RING SIZE WITH I<sup>131</sup>  
LABELLED KI. II\***

**Solvent Effect in Ethanol. Anomalous Exchange Reaction of c-Butyl Iodide in  
Different Solvents**

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The exchange reactions of c-pentyl, c-hexyl, c-heptyl, c-octyl and 2-methyl-c-hexyl iodides with I<sup>131</sup> labelled KI were studied in absolute ethanol at different temperatures. The exchange reactions of c-butyl iodide were studied at different temperatures in absolute ethanol, dimethylformamide and dimethyl sulfoxide as solvents. The kinetic data and activation constants obtained were brought into correlation with the solvent effect and with the change in the ring size of the cycloalkyl iodides. It was found that changes in the dielectric constant do not affect the rates of the exchange reactions in a clear-cut way. In ethanol H-bonding probably plays an important role. The investigations show that there is an anomaly in the exchange reactions of c-butyl iodide.

In investigations of the relation between molecular structure and reactivity, the study of exchange reactions provides characteristic data. Several authors have studied the external factors: the effect of the solvent or of the solvent mixture [1—3], and the effects of proton-containing solvents [4, 5] for different homologous series.

For the comparison of the c-alkane homologous series, in the main physical measurements describing the ground states of the molecules, calculations concerning their symmetries have been applied. The aim of our investigations was to study the effect of the molecular structure on the reaction under substitution reaction conditions, and to find a connection between these and the various experimental and calculable constants and parameters.

In an earlier communication [6] we reported data on the exchange reactions of c-pentyl, c-hexyl, c-heptyl, c-octyl and 2-methyl-c-hexyl iodides with labelled KI, and with dimethylformamide and dimethyl sulfoxide as solvents. The present paper summarizes the data referring to ethanol, a strongly solvating proton-containing solvent, and supplies the studies concerning the homologous series with data on the exchange reactions of c-butyl iodide. For the correlation with the molecular structure, the activation energies, activation free enthalpies and activation entropies referring to the activation state of the reaction were determined under different reaction conditions. The experimental results obtained and partly reported are brought into relation with the molecular structures of the hydrocarbons of different ring size.

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### Experimental methods

The method of measuring the kinetic data of the exchange reactions in the present investigation was described in our previous paper [6]. The *c*-alkyl iodides necessary for the study were prepared with methods described in the literature, purified on the basis of their physical constants and checked chromatographically.

The activities of the solutions were measured with a scintillation detector using of a hollow gamma-crystal.

### Experimental results and discussion

#### 1. Exchange reaction in absolute ethanol

For the individual *c*-alkyl iodides the specific activity values measured in a benzene phase for the exchange reaction, and those arising from the incorporation of the labelled iodide, refer to initial reaction mixtures of identical activities. The kinetic curves for *c*-pentyl and *c*-octyl iodides were linear; they were of saturation type for *c*-heptyl and 2-methyl-*c*-hexyl iodides. It was not possible to observe an exchange in the case of *c*-hexyl iodide in ethanol. The reactions were carried out in the temperature range 65–80°C; the extent of the exchange increased with increasing temperature.

Table I

	°C	$W_0$ mole · l <sup>-1</sup> · sec <sup>-1</sup>	$k$ mole <sup>-1</sup> · l · sec <sup>-1</sup>	$E$ kcal · mole <sup>-1</sup>	$\Delta S^\ddagger$ cal · mole <sup>-1</sup> · degree <sup>-1</sup>	$\Delta G^\ddagger$ kcal · degree <sup>-1</sup>
<i>c</i> -pentyl iodide	65	$6.5 \cdot 10^{-8}$	$2.62 \cdot 10^{-4}$	18.1	-21.2	25.3
	70	$9.7 \cdot 10^{-8}$	$3.90 \cdot 10^{-4}$		-21.4	25.5
	75	$15.0 \cdot 10^{-8}$	$6.00 \cdot 10^{-4}$		-21.5	25.6
<i>c</i> -heptyl iodide	65	$0.9 \cdot 10^{-7}$	$3.50 \cdot 10^{-4}$	17.2	-23,2	25.2
	70	$1.2 \cdot 10^{-7}$	$4.90 \cdot 10^{-4}$		-23.7	25.4
	75	$1.8 \cdot 10^{-7}$	$7.30 \cdot 10^{-4}$		-23,8	25.9
<i>c</i> -octyl iodide	70	$2.4 \cdot 10^{-8}$	$0.96 \cdot 10^{-4}$	19.4	-20.5	26.3
	75	$3.8 \cdot 10^{-8}$	$1.50 \cdot 10^{-4}$		-20.6	26.6
	80	$5.3 \cdot 10^{-8}$	$2.17 \cdot 10^{-4}$		-20.6	26,7
2-methyl- <i>c</i> -hexyl iodide	70	$1.7 \cdot 10^{-8}$	$0.68 \cdot 10^{-4}$	20.7	-17.1	26.5
	75	$2.7 \cdot 10^{-8}$	$1.08 \cdot 10^{-4}$		-17.1	26.6
	80	$4.2 \cdot 10^{-8}$	$1.60 \cdot 10^{-4}$		-17.2	26.7

From a comparison of the experimental results with the dielectric constants of the solvents used (25.8 for ethanol, 39.0 for dimethylformamide, and 46 for dimethyl sulfoxide) and with the solvent effects observed for  $S_N2$  reactions [7], it was to be expected that, since the reaction rate is decreased by the use of a more polar solvent, the exchange reaction would be the greatest in ethanol, less in dimethylform-

amide, and even less in dimethyl sulfoxide. The experiments showed that the exchange was the greatest in dimethylformamide, less in dimethyl sulfoxide, and the least in ethanol. If only the dielectric constants were taken into account, this would mean an anomaly with regard to ethanol as solvent. Ethanol is a proton-containing solvent and belongs to the most strongly solvating solvents, while the other two are of aprotic nature. The lower rate obtained in ethanol clearly indicates that in this solvent the primary factor is the specific interaction between the anions and the ethanol molecules, the hydrogen-bond. Therefore the ordering of the system is more extensive, and the internal energy is lower than that to be expected on the basis of the dielectric constant. The initial rate values, the rate coefficients and the activation data for the reactions carried out in absolute ethanol at different temperatures are given in Table I.

## 2. Exchange reactions of *c*-butyl iodide

The exchange reactions of *c*-butyl iodide were studied in all three solvents, at different temperatures, under the conditions described in the previous paper. The kinetic curves in dimethylformamide and in dimethyl sulfoxide pass through maxima. The positions of the maxima shifted towards shorter reaction times with the increase of temperature. The elimination accompanying the substitution in dimethyl-

Table II

	°C	dimethyl- formamide	dimethyl sulfoxide	ethanol
$W_0$ (mole · l <sup>-1</sup> · sec <sup>-1</sup> )	55 65 75	13.6 · 10 <sup>-6</sup> 25.7 · 10 <sup>-6</sup> 46.6 · 10 <sup>-6</sup>	6.5 · 10 <sup>-6</sup> 13.3 · 10 <sup>-6</sup> 28.2 · 10 <sup>-6</sup>	— 0.8 · 10 <sup>-6</sup> 1.7 · 10 <sup>-6</sup>
$k$ (mole <sup>-1</sup> · l · sec <sup>-1</sup> )	55 65 75	5.46 · 10 <sup>-2</sup> 9.33 · 10 <sup>-2</sup> 18.60 · 10 <sup>-2</sup>	2.60 · 10 <sup>-2</sup> 5.33 · 10 <sup>-2</sup> 11.30 · 10 <sup>-2</sup>	— 3.38 · 10 <sup>-3</sup> 6.83 · 10 <sup>-3</sup>
$E$ (kcal · mole <sup>-1</sup> )		15.5		16.7
$\Delta S^\ddagger$ (cal · mole <sup>-1</sup> · degree <sup>-1</sup> )	55 65 75	-17.3 -17.4 -17.4	-18.3 -18.4 -18.4	— -20.8 -20.9
$\Delta G^\ddagger$ (kcal · degree <sup>-1</sup> )	55 65 75	21.7 21.9 22.1	22.0 22.2 22.4	— 23.7 24.0

formamide became dominant already from the fifth minute. In ethanol saturation curves were obtained. The data calculated from the experimental results obtained are given in Table II.

The kinetic and activation data obtained in the three solvents at different temperatures were brought into correlation with the ring size and with the internal struc-

tures of the molecules.  $S_N2$  reactions involve a reversible  $sp^3 \rightarrow sp^2$  electron shell hybridization in the transition state. The strain theory of BROWN [8], which takes into account the extent of steric strain in the arrangement of the  $sp^2$  and  $sp^3$  shells and explains the inhibited or favoured natures of the  $sp^3 \rightarrow sp^2$  and  $sp^2 \rightarrow sp^3$  reactions on this basis, is applicable to cyclic systems.

In cyclic systems the hybridization of the bond is accompanied by angular strain, torsional strain and ring deformation. These changes may be either favourable or unfavourable with respect to the reaction.

In the case of small, three and four-membered rings, the angular strain being high any change results in a significant deformation. In the cyclobutane system the normal bond angle is  $90^\circ$ , which shows a smaller decrease from the tetrahedral bond angle ( $109^\circ 28'$ ) than from the trigonal bond angle ( $120^\circ$ ), i. e. the  $sp^3$  electron distribution is more favoured than the  $sp^2$ . This phenomenon can be affected by other factors. The kinetic data obtained by us also show differences from those expected on the basis of the theory. In the case of *c*-butyl iodide the activation entropy values are significantly decreased, and are less negative compared with those of the other compounds, although on the basis of the  $w_0$  values the largest negative activation entropy values were to be expected here. A comparison of our results with the experimental results obtained by other authors for similar systems [9, 10] permits the conclusion that in the case of the *c*-butyl iodide, as a result of the stabilizing effects of the polar solvents, a carbonium ion complex is formed in advance, at least in part, and this takes part in the substitution reaction.

In the five and seven-membered rings the torsional strain predominates: in the case of cyclopentane, if a planar system is assumed there are oppositions of ten C—H bonds, which result in a torsional strain of about  $10 \text{ kcal} \cdot \text{mole}^{-1}$ . Since the molecule is puckered, the total strain is less. On any carbon atom the electron transfer  $sp^3 \rightarrow sp^2$  results in a decrease of the strain energy to a value of  $4 \text{ kcal} \cdot \text{mole}^{-1}$ . This means that the substitution reactions of the *c*-pentane systems are relatively fast. Similar conclusions can be drawn for the *c*-heptane ring, which is likewise a mobile and closed system, although the opposition of the corresponding C—H bonds is of somewhat less importance than for the five-membered rings.

In the six-membered rings the chair-form is free of the bond opposition. The change of the hybridization from  $sp^3$  to  $sp^2$  brings about the bond opposition, this increases the internal energy, and as a result the substitution reactions are slow in the *c*-hexyl systems.

The *c*-octane skeleton is a closed system with angular deformation, bond opposition and ring deformation: since the number of C—H bonds taking part in the opposition will be smaller, the  $sp^2$  configuration is more favoured than the  $sp^3$  arrangement, and this increases the rate of the substitution reaction.

On the basis of the experimental results, in the case of the homologous series investigated, the rate of the bimolecular nucleophilic substitution decreases in the following order: *c*-butyl iodide > *c*-pentyl iodide > *c*-heptyl iodide > *c*-octyl iodide > > *c*-hexyl iodide > 2-methyl-*c*-hexyl iodide.

This order of the reaction rates is in agreement with both the regularities of the external effects exerted on the reaction and the physical data expected on the basis of the steric structure of the molecule.

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ИЗУЧЕНИЕ РЕАКЦИЙ ЗАМЕЩЕНИЯ РАЗЛИЧНЫХ ЦИКЛИЧЕСКИХ  
АЛКИЛЙОДИДОВ МЕЧЕННЫХ ЙОДИСТЫМ КАЛИЕМ. II.

*Влияние этанола как растворителя. Аномальные реакции замещения циклобутильодида в различных растворителях*

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Исследовались реакции замещения циклопентил-, циклогексил-, циклогептил-, циклооктил-2-метил-циклогексилйодида меченных йодистым калием (I<sup>131</sup>) в среде абсолютного этанола при разных температурах. Реакции замещения циклобутильодида изучены также в среде диметилформамида и диметилсульфоксида. Обнаружена корреляция между числом членов цикла и природой растворителей с одной стороны и полученными кинетическими характеристиками и константами активации — с другой. Показано отсутствие прямой связи между величиной диэлектрической постоянной среды и скоростью реакций замещения. Большое значение имеют, по-видимому, водородные связи на кинетику реакций в среде этанола. Для реакций замещения циклобутильодида при любых условиях обнаружены аномалии.