

INVESTIGATION OF THE EXCHANGE REACTIONS
OF *c*-ALKYL IODIDES OF DIFFERENT RING SIZE WITH
¹³¹I LABELLED POTASSIUM IODIDE

By

F. SIROKMÁN and É. HAJDU

Institute of Radiochemistry, Attila József University, Szeged

(Received December 1, 1970)

Exchange reactions of *c*-pentyl iodide, *c*-hexyl iodide, 2-methyl-*c*-hexyl iodide, *c*-heptyl iodide, *c*-octyl iodide with ¹³¹I labelled potassium iodide in dimethylsulfoxide and dimethylformamide solvents were investigated at various temperatures. It has been found that the rate of exchange is lower in the more polar solvent, the calculated energy of activation being, however, constant for a given compound in both solvents. The thermodynamic constants, entropy of activation, and free enthalpy of activation of the reaction have been determined. A correlation between the rates of exchange reactions and the ring size was found.

The investigation of the isotope-exchange reactions and the co-ordination of exchange data with the molecular structure have been performed in case of several compounds. The factors determining the exchange reaction were investigated in different compounds. The exchange reactions of some homologous series were studied, *e.g.* with labelled iodide ions [1]. In some cases the dependence of exchange reaction on temperature was investigated in various solvents [2]. The exchange reactions with iodine molecules have been studied by using labelled iodine [3]. The examination of the iodide ion exchange of *c*-alkyl halides and *o*-substituted *c*-alkyl halides gives information on the exchange of *equatorial* and *axial* halogen atoms. In this field, STEVENS and co-workers [4], investigating the exchange of covalent iodine in 6,4-di-desoxy-2,3-dibenzyl-4,1- α -methyl-galactopyranose, in which the conformation conditions of the pyranose ring correspond to those of the *c*-hexane skeleton, have ascertained that the compound which proved to contain *axial* iodine gives 6,4-di-desoxy-2,3-dibenzyl-4,1- α -metoxi-glucopyranose with Walden inversion, its reaction rate being 2.8 times higher than that of the inverse reaction in which the iodine is *equatorial*. Investigating the exchange reaction of the optically active 2-iodine-octane with Walden inversion, it was established that the reaction is bimolecular and the reaction rate depends on KI concentration [5]. The reaction mechanism has been discussed in detail by INGOLD [6].

Although there have been studies of iodide ion exchange reactions in the literature, the study of the iodide ion exchange reaction of *c*-alkyl halides of different ring size and of *o*-substituted *c*-alkyl halides requires more attention. It has been decided to examine the influence of the ring size on the exchange reaction in solvents

of different polarity and its dependence on temperature. The effect exerted on the exchange reaction by the *o*-substituents influencing the stability of different conformational isomers, which can be demonstrated on the basis of exchange, may be the topic of further experiments. The relations between the effect of the solvent polarity on the reaction rate and molecular structure and solvation may be studied with the aid of the determination of activation energy.

Experimental

Having prepared the compounds to be investigated: *c*-pentyl iodide, *c*-hexyl iodide, 2-methyl-*c*-hexyl iodide, *c*-heptyl iodide, *c*-octyl iodide [7], their purity has been tested by their physical constants. The exchange reactions were carried out between 55 and 85 °C, in sealed tubes placed in an ultrathermostat. The concentration of *c*-alkyl iodides was 0.01 M and the KI¹³¹ labelled potassium iodide was used in 2.5-fold excess. The exchange reactions were investigated in dimethylsulfoxide ($\epsilon=46$) and dimethylformamide ($\epsilon=39$). 5 ml from each reagent dissolved in those solvents were placed in bomb tubes. After definite periods of time, samples were taken and the reactions were stopped by a salt and ice mixture. The organic iodide was separated from the potassium iodide by means of benzene extraction and the benzene phase was washed by 3×10 ml distilled water. Both phases were completed to identical volumes, 5 ml of each solution were placed into test tubes and the activity was measured by a NK—108 scaler with a hollow γ -crystal. The

increasing activity values of the *c*-alkyl iodides in the benzene phase were used for the calculations.

Table I

	Temp. °C	k l·mole ⁻¹ ·s ⁻¹	
		dimethyl- formamide	dimethyl- sulfoxide
<i>c</i> -pentyl iodide	55	$0.77 \cdot 10^{-2}$	$0.34 \cdot 10^{-2}$
	65	$1.60 \cdot 10^{-2}$	$0.68 \cdot 10^{-2}$
	75	$3.13 \cdot 10^{-2}$	$1.33 \cdot 10^{-2}$
<i>c</i> -hexyl iodide	55	$1.55 \cdot 10^{-4}$	$0.78 \cdot 10^{-4}$
	65	$3.77 \cdot 10^{-4}$	$2.05 \cdot 10^{-4}$
	75	$8.55 \cdot 10^{-4}$	$4.38 \cdot 10^{-4}$
<i>c</i> -heptyl iodide	55	$0.61 \cdot 10^{-2}$	$0.48 \cdot 10^{-2}$
	65	$1.27 \cdot 10^{-2}$	$1.00 \cdot 10^{-2}$
	75	$2.50 \cdot 10^{-2}$	$1.95 \cdot 10^{-2}$
<i>c</i> -octyl iodide	55	$2.46 \cdot 10^{-3}$	$1.44 \cdot 10^{-3}$
	65	$5.52 \cdot 10^{-3}$	$3.26 \cdot 10^{-3}$
	75	$10.50 \cdot 10^{-3}$	$6.32 \cdot 10^{-3}$
2-methyl- <i>c</i> -hexyl iodide	55	$3.99 \cdot 10^{-4}$	$1.91 \cdot 10^{-4}$
	65	$10.00 \cdot 10^{-4}$	$5.41 \cdot 10^{-4}$
	75	$26.96 \cdot 10^{-4}$	$13.98 \cdot 10^{-4}$
	85	$69.06 \cdot 10^{-4}$	$30.95 \cdot 10^{-4}$

Experimental results and discussion

The specific activity values calculated from the measured data were related to a starting reaction mixture of defined activity. The isotopic effect in the exchange may be neglected, the inactive and active iodide ions are exchanged with the same probability [5], therefore, the reaction can be followed by measuring the changes in activity.

Two different types of curves have been obtained: one of them exhibits the character of a saturation curve,

the other goes through a maximum. Curves of saturation character have been obtained with *c*-hexyl iodide (Fig. 1), 2-methyl *c*-hexyl iodide in both solvents and with *c*-octyl iodide in dimethylformamide; curves with a maximum with *c*-pentyl iodide and *c*-heptyl iodide (Fig. 2) in both solvents and with *c*-octyl iodide in dimethylsulfoxide.

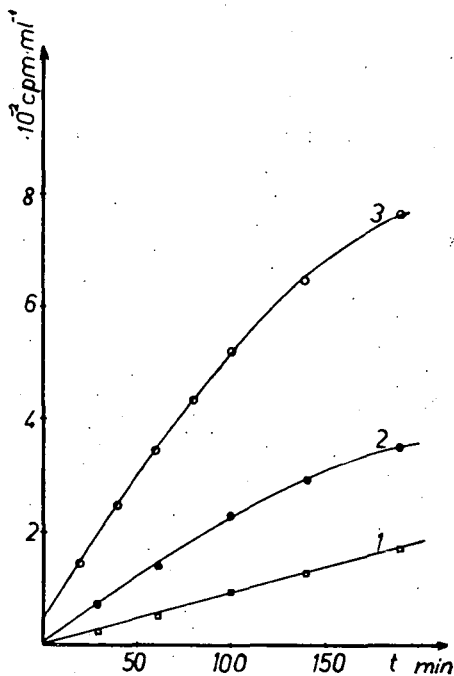


Fig. 1. Kinetic curves of *c*-hexyl iodide in dimethylformamide:
1: 55 °C; 2: 65 °C; 3: 75 °C

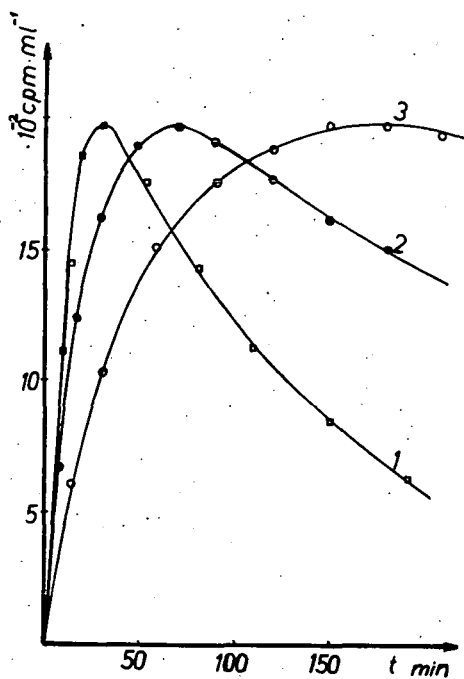


Fig. 2. Kinetic curves of *c*-heptyl iodide in dimethylformamide:
1: 55 °C; 2: 65 °C; 3: 75 °C.

The presence of a maximum shows that the exchange reaction is accompanied by elimination. By increasing the temperature, the maxima appear after shorter reaction times, but the degree of exchange corresponding to the maxima is unchanged.

The values of the initial rate were determined from the kinetic curves. According to previous investigations [6] these exchange reactions are second order processes.

$$w = k[RI][KI]. \quad (1)$$

On the basis of this theory, the values of the rate constants were calculated (Table I) from the initial rates determined from the kinetic curves. Activation energy values were determined from the temperature dependence of the rate constants according to the Arrhenius equation (Figs. 3 and 4). The activation energies for the same compound in different solvents proved to be identical (Table II).

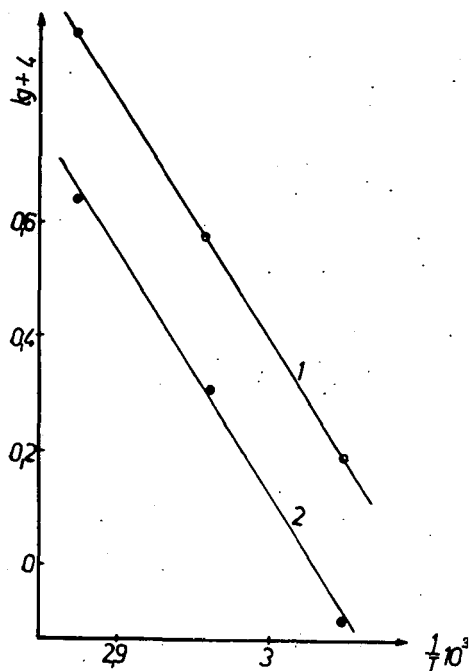


Fig. 3. Temperature dependence of k for c-hexyl iodide: 1: in dimethylformamide; 2: in dimethylsulfoxide.

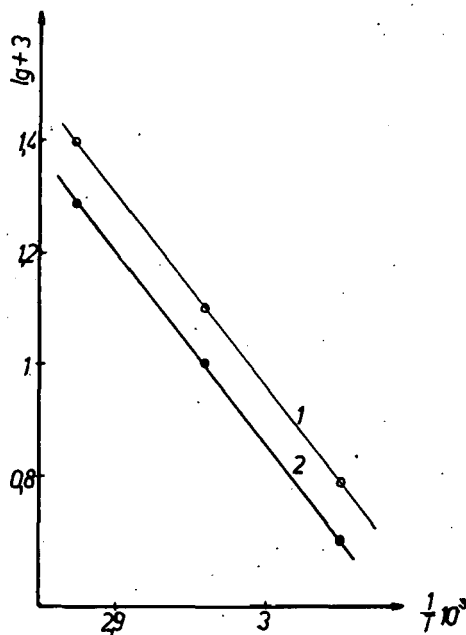


Fig. 4. Temperature dependence of k for c-heptyl iodide: 1: in dimethylformamide; 2: in dimethylsulfoxide.

Since the activation energy of the exchange reaction for a compound is not affected by changing the solvent, the reason of the changes in the reaction rate is to be attributed to the change in the value of the pre-exponential factors. The values of the pre-exponential factors are given in Table III.

● Apart from the possible change in the transmission coefficient $\eta = 1$, the change of the pre-exponential factors may be caused by the change in the entropy of activa-

Table II

	E kcal·mole ⁻¹
c-pentyl iodide	15.86
c-hexyl iodide	19.66
c-heptyl iodide	16.00
c-octyl iodide	17.16
2-methyl-c-hexyl iodide	20.80

Table III

	A l·mole ⁻¹ ·s ⁻¹	
	dimethyl- formamide	dimethyl- sulfoxide
c-pentyl iodide	$2.93 \cdot 10^8$	$1.26 \cdot 10^8$
c-hexyl iodide	$1.95 \cdot 10^9$	$1.06 \cdot 10^9$
c-heptyl iodide	$2.83 \cdot 10^8$	$2.24 \cdot 10^8$
c-octyl iodide	$6.68 \cdot 10^8$	$3.98 \cdot 10^8$
2-methyl-c-hexyl iodide	$3.09 \cdot 10^{10}$	$1.51 \cdot 10^{10}$

tion. The entropy values of activation,

$$A = \eta \frac{kT}{h} e^{\frac{\Delta S^\ddagger}{R}} \quad (2)$$

given in Table IV, were obtained on this basis.

The free enthalpy of activation of the exchange reaction (Table IV) was calculated from the known thermodynamic relation

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (3)$$

Table IV

	Temp. °C	ΔS^\ddagger cal·mole ⁻¹ ·deg ⁻¹		ΔG^\ddagger kcal·deg ⁻¹	
		dimethyl- formamide	dimethyl- sulfoxide	dimethyl- formamide	dimethyl- sulfoxide
c-pentyl iodide	55	-19.98	-21.65	22.41	22.96
	65	-20.037	-21.715	22.63	23.20
	75	-20.095	-21.770	22.85	23.46
c-hexyl iodide	55	-16.21	-17.42	24.98	25.37
	65	-16.27	-17.48	25.16	25.57
	75	-16.33	-17.54	25.34	25.76
c-heptyl iodide	55	-20.05	-20.51	22.58	22.73
	65	-20.105	-20.57	22.79	22.95
	75	-20.16	-20.63	23.02	23.18
c-octyl iodide	55	-18.34	-19.37	23.18	23.51
	65	-18.40	-19.43	23.38	23.73
	75	-18.46	-19.49	23.58	23.94
2-methyl-c-hexyl iodide	55	-10.73	-12.14	24.34	24.80
	65	-10.78	-12.20	24.46	24.94
	75	-10.84	-12.26	24.59	25.09
	85	-10.90	-12.32	24.72	25.23

By comparing the data, it can be seen that the activation energies are the highest in the case of c-hexyl iodide and of 2-methyl-c-hexyl iodide. This may be attributed to the comparatively slow reaction of the *equatorial* iodine in the c-hexane ring, in agreement with the results of STEVENS and co-workers [4]. The lower activation energy values obtained for the other three members of the homologous series are to be explained by the conformations of the rings. Similar differences are found by calculating the combustion heat of a methylene group in different cycloalkanes [8].

References

- [1] *McKay, H. A. C.*: Nature, **139**, 283 (1937).
- [2] *Dutka, F. D. Gál*: M. T. A. Kém. Tud. Oszt. Közl. **11**, 2 (1959).
- [3] *Körös, E., M. Orbán, A. Mesztizky*: Magyar Kémiai Folyóirat **74**, 103 (1968).
- [4] *Stevens, C. L., K. G. Taylor, J. Valicenti*: J. Amer. Chem. Soc. **87**, 4579 (1965).
- [5] *Hughes, E. D., F. Juliusburger, S. Marterman, B. Tapley, J. Weiss*: J. Chem. Soc. **1935**, 1525.
- [6] *Ingold, C. K.*: Structure and Mechanism in Organic Chemistry, 2nd Ed., Cornell University Press, Ithaca and London, 1969, p. 423.
- [7] *Vogel, A. I.*: Practical Organic Chemistry, 3rd Ed., Longmans, Green and Co., London, 1956, p. 285.
- [8] *Eliel, E. L.*: Stereochemistry of Carbon Compounds, McGraw-Hill Book Co., Inc., New York, (1962), p. 189.

ИССЛЕДОВАНИЕ ОБМЕННЫХ РЕАКЦИЙ ЙОДИСТА ЦИКЛОАЛКИЛОВОГО
РАЗЛИЧНЫМ ЧИСЛОМ АТОМОВ УГЛЕРОДА
КОЛЬЦА С ЙОДИСТЫМ КАЛИЯ НАМЕЧЕННЫМ C^{131}

Ф. Широ́кман, Е. Ха́йду

Авторы исследовали обменные реакции йодиста циклопентилового-циклогексилового-2-метилциклогексилового-циклооктилового-циклогептилового с йодистым калия намеченным с C^{131} при различной температуры в растворителях диметилсульфоксида и диметилформамида. Было установлено, что степень обмена является меньше в полярных растворителях, однако рассчитанная энергия активации оказалась постоянной при обеих растворителях. Были определены термодинамические постоянные реакций — энтропия и свободная энталпия активации. По опытам нашлось соотношение между скоростями обменных реакций и числом атомов углерода кольца.