ANIONIC *cis-trans* ISOMERISATION OF DIMETHYL PERFLUORO-(4-METHYL-2-PENTENE)DIOATE*

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Potassium fluoride induced *cis-trans* isomerisation of the title compound *I* was investigated. The isomerisation takes place in a heterogeneous system and is enabled by solvation effect of dipolar aprotic solvents. Dimethyl 2,3,3,4-tetrafluoro-2-trifluoromethylpentanedioate (*II*) is formed as side product by proton transfer from the solvent to the intermediate 1,3-bis(methoxycarbonyl)-perfluoro-1-butanide (*III*). The mechanism was deduced from the reaction conditions and results of the isomerisation. Composition of the equilibrium mixture of *cis*- and *trans*-isomer (*Ia*, *Ib*, respectively) studied in the interval 2—75°C, shows an extreme. In the interval 2—30°C the reaction $Ia \rightarrow Ib$ appears to be exothermic ($\Delta H = -21 \cdot 2 \text{ kJ mol}^{-1}$), in the interval 35—47°C the enthalpy equals practically zero and in the maximum of the curve at 42·5°C the entropic factor $\Delta S = 2 \cdot 82 \text{ J mol}^{-1} \text{ K}^{-1}$. In the interval 50—75°C the reaction is endothermic ($\Delta H = 15 \cdot 2 \text{ kJ mol}^{-1}$). In this context the effect of steric interactions between the substituents $-COOCH_3$ and $-CF(CF_3)COOCH_3$, as well as of the so called *cis*-effect in 1,2-dihalogenoethylenes, on the $Ia \rightleftharpoons Ib$ equilibrium are discussed.

Oligomerisation of perfluoroolefins[1-7] and derivatives of perfluoroalkenoic acids[8-10] leads to products with double bond in the chain which can give rise to configurational isomerism. The proportion of the arising configurational isomers has been studied for the oligomerisation of hexafluoropropene[5-7,11-14] and dimerisation of trifluoropropenoic acid derivatives[10,15]. As far as we know, *cis-trans* isomerisations of the mentioned oligomerisation products have not been studied in detail as yet. We have found previously[10] that dimethyl perfluoro(4-methyl-2-pentene)-dioate (*I*), formed by potassium fluoride catalysed dimerisation of methyl trifluoropropenoate, represents a mixture of *cis*- and *trans*-isomer (*Ia* and *Ib*, respectively). In acetonitrile, nitrobenzene or diethylene glycol dimethyl ether, the ratio of the isomers *Ia* and *Ib* was independent of time whereas in dimethyl sulfoxide it showed a dependence, but only if the mixture contained undissolved potassium fluoride. This effect, indicating a subsequent *cis-trans* isomerisation of the dimer *I*, is the subject of the present communication.

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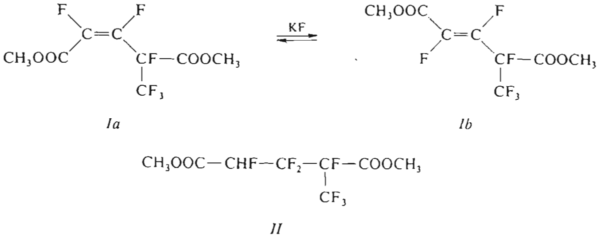
Conditions of the potassium fluoride induced *cis-trans* isomerisation of *I* were investigated starting from both the isomers *Ia*, *Ib*. Their interconversion took place only in the presence of undissolved potassium fluoride and it was detectable only in dipolar aprotic solvents such as dimethyl sulfoxide, tetrahydrothiophene 1,1-dioxide or hexamethylphosphoric triamide. In acetonitrile no isomerisation was observed but when this solvent was mixed with about 10% of dimethyl sulfoxide the reaction was detectable. The qualitative results are given in Table I.

From the isomerisation mixture we isolated dimethyl 2,3,3,4-tetrafluoro-2-trifluoromethylpentanedioate (*II*) as a side product. This compound was not formed when the dimerisation of methyl trifluoropropenoate[10] was carried out in acetonitrile, nitrobenzene or diethylene glycol dimethyl ether. A small amount of *II* (about 3·5%) was formed in the dimerisation of dimethyl sulfoxide for prolonged



SCHEME 1

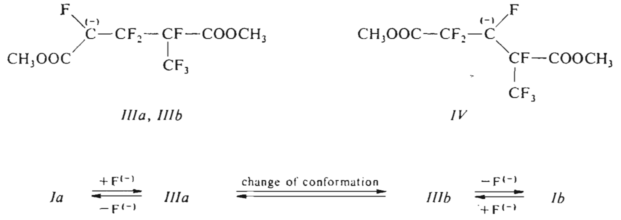
TABLE I

Conditions and Results of the Potassium Fluoride Induced *cis-trans* Isomerisation of the Dimer *I*

Solvent[a]	KF g (mg l^{-1})	Form of KF	Temperature °C	Isomerisation
Dimethyl sulfoxide	(15·1)[b]	solution	25—60	no reaction
Dimethyl sulfoxide[c]	0·6	suspension	20—70	isomerisation
Acetonitrile	(~10)[b]	solution	40	no reaction
Acetonitrile	0·8	suspension	40	no reaction
Acetonitrile–dimethyl sulfoxide[d]	0·8	suspension	25—40	very slow

[a] A mixture of 25 ml solvent and 1 g (3·57 mmol) *Ia*, *Ib* or their mixture; [b] determined after evaporation of 100 ml saturated solution at 25°C; [c] at 20°C, 1% (vol.) acetonitrile; [d] 89 : 11 (vol.).

period of time if the mixture contained undissolved potassium fluoride. The content of the isomers *Ia* and *Ib* in the equilibrium mixture was determined by performing the reaction with the individual isomers and making an asymptote to the time dependence curves (Fig. 1, curves *1* and *3*). With increasing amount of potassium fluoride the isomerisation was faster (Fig. 1, curves *2* and *3*). We have also proved that starting from any mixture of *Ia* and *Ib* we can reach the equilibrium if the previously mentioned reaction conditions are observed. The values are reproducible within the experimental error (±3% rel.). The equilibrium mixture composition data are given in Fig. 2.



SCHEME 2

EXPERIMENTAL

The temperature data are uncorrected. Gas-liquid chromatography was carried out on a Chrom 4 chromatograph (Laboratorní přístroje, Prague; flame ionization detector, integrator, column diameter 0·3 cm, Chromaton N-AW-DMCS, Lachema, Brno). Preparative gas-liquid chromatography was performed on a modified Chrom 2 instrument (flame ionisation detector, 500 cm column of 1 cm diameter). The NMR spectra were taken on a Varian XL-100-15 (Palo Alto) instrument (deuteriochloroform, chemical shifts in ppm, for ^{19}F-NMR spectra internal standard CCl_3F; s singlet, d doublet, t triplet, q quartet, m multiplet.).

Reagents: Dimethyl sulfoxide, tetrahydrothiophene 1,1-dioxide, hexamethylphosphoric triamide and acetonitrile were purified according to ref.[16,17] and dried over molecular sieve Potasit 3 (J. Dimitrov Chemical Works, Nováky, Czechoslovakia). Potassium fluoride of analytical purity (Lachema) was heated in a platinum dish to 300—400°C and then dried for 8 h at 120°C and 1·3 Pa. Dimethyl perfluoro(4-methyl-2-pentene)dioate (*I*) was prepared as a mixture of *cis*-(*Ia*) and *trans*-isomer (*Ib*) according to ref.[10]. The configurational isomers *Ia* and *Ib* were separated by gas-liquid chromatography (15% poly(butanediol succinate), 170°C) and their purity was 99·0 and 99·5%, respectively (gas-liquid chromatography: 15% Carbowax 6000, 240 cm column, 190°C). The separated isomers were stored at dry ice temperature.

Rate and equilibrium composition determination: A sample of the reaction mixture (0·2—0·4 ml) was mixed with a twofold volume of a solution of lanthanum nitrate in dimethyl sulfoxide and kept in dry ice for 1 min. Prior to analysis the sample was shaken with a a mixture of water (2 ml) and 1,1,2-trichlorotrifluoroethane (Ledon 113; 1 ml). The oily layer was dried over anhydrous sodium sulfate (for gas–liquid chromatography, *vide infra*). The reaction mixture was prepared in dry atmosphere, potassium fluoride was ground manually, was not sieved and its specific surface was not determined.

cis-trans-Isomerisation of Dimethyl Perfluoro(4-methyl-2-pentene)dioate (*I*)

A) A mixture of potassium fluoride (Fig. 1), *cis*-(*Ia*) or *trans*-(*Ib*) dimer (0·705 g; 2·5 mmol) and dimethyl sulfoxide (30 ml) was stirred under exclusion of moisture so that the solid phase was dispersed. The samples were processed as described above. Gas–liquid chromatographic analysis was carried out on poly(butanediol succinate), 120 cm column, 170°C.

B) A mixture of potassium fluoride, the isomer *Ia* or *Ib* (Table I) and the solvent (25 ml; Fig. 2) was stirred with exclusion of moisture so that the solid phase was dispersed. The withdrawn samples were immediately analysed by gas–liquid chromatography (poly(1,3-propandiol sebacate), 250 cm column, 160°C).

Dimethyl 2,3,3,4-Tetrafluoro-2-trifluoromethylpentanedioate (*II*)

The reaction mixture from isomerisation of the dimer *I* in dimethyl sulfoxide was diluted with 1,1,2-trichlorotrifluoroethane (20 ml), washed with water, dried over anhydrous magnesium sulfate, distilled and subjected to preparative gas–liquid chromatography on Carbowax 6000 (163°C). IR spectrum (tetrachloromethane), cm^{-1}: 1049 m, 1079 s, 1162 s, 1193 s, 1240 s,

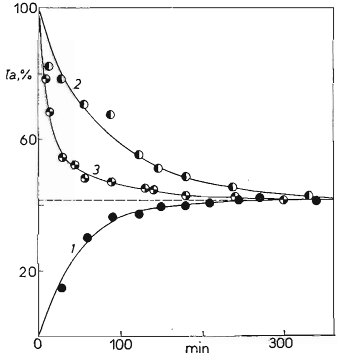


Fig. 1

Time Dependence of Isomerisation of the Dimer *I* at 40°C

1 Starting from *trans*-isomer *Ib* (46 mg, 0·79 mmol, KF); 2 starting from *cis*-isomer *Ia* (81 mg, 1·4 mmol, KF); 3 starting from *Ia* (160 mg, 2·75 mmol, KF).

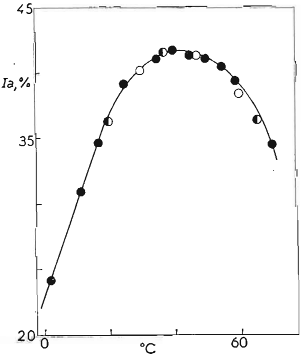


Fig. 2

Content of *cis*-Isomer *Ia* in the Equilibrium Mixture in *cis-trans* Isomerisation of the Dimer *I*

● Dimethyl sulfoxide: ○ tetrahydrothiophene 1,1-dioxide; ◐ hexamethylphosphoric triamide.

1272 s, 1295 s, 1325 m, 1360 s, 1438 m; 1763 s, 1773 s ν(C=O), 2858 w, 3020 w. ^{1}H-NMR spectrum: dt 5·43, $^2J_{HF}$ 46, $^3J_{HF}$ 9 (—CHF—CF$_2$); s 3·87 (OCH$_3$). ^{19}F-NMR spectrum: d —64, $^3J_{FF}$ 14 (CF$_3$); dd —82·7 (CF$_2$); q —146·3, $^3J_{FF}$ 10 (CF); dm —205·8 (CHF). For $C_8H_7F_7O_4$ (300·1) calculated. 32·01% C, 2·35% H, 44·31% F; found: 32·12% C, 2·36% H, 44·93% F.

DISCUSSION

The reaction conditions for the dimerisation of methyl trifluoropropenoate[10] and the *cis-trans* isomerisation of its dimer *I* differ in the following factors: The latter isomerisation proceeds in aprotic dipolar solvents and only in the presence of undissolved potassium fluoride. Since the isomerisation is a catalysed reaction, its mechanism must involve at least one intermediate which arises by reaction of the starting compound *I* with potassium fluoride. On the basis of previous discussions[1–10] we can assume a carbanion character of such intermediate. Formation of the derivative *II* during the isomerisation confirms that an intermediate of the type *III* is involved. As follows from the structure of *II*, the fluoride ion adds to the double bond of *I* preferably *via* the carbanion *III* which is stabilized by the COOCH$_3$ group, and not *via* the alternative species *IV*. This at the same time shows that this group has a stronger stabilizing effect than a perfluoroalkyl group, as discussed by us previously[10]. The fact that the presence of undissolved potassium fluoride is essential and that its amount affects the reaction rate (Table I, Fig. 1) indicates a reaction which takes place on, or in the vicinity of, the catalyst surface. Similar effects were observed in isomerisations of fluoroolefins by alkali metal fluorides[18,19] and also in the addition of fluorinated ketone to alkenes[20]. The fact that the isomerisation takes place in a certain solvent type shows a specific solvation effect. The difficult formation of the intermediate *III* is in accord with its instability and rapid intramolecular transformation during the dimerisation[10].

We may thus formulate the main steps of the *cis-trans* isomerisation of the compound *I* as shown in Scheme 2. The isomerisation which, contrary to the dimerisation, is a reversible reaction, must involve – according to the microscopic reversibility principle[18] – common intermediates for both the reaction pathways. On the catalyst surface, the *cis*-isomer *Ia* affords by the action of solvation forces the carbanion *IIIa* the geometry of which is close to that of transition state of the *syn-* or *anti*-elimination, leading to *Ia* (ref.[10]). Conformational change of *IIIa* affords the structure *IIIb*, similar to the transition state which on *anti-* or *syn*-elimination of the fluoride ion gives the *trans*-isomer *Ib*. The reverse reaction will proceed along the analogous pathway.

In the studied interval 2–70°C, the plot of the equilibrium composition of the mixture of configurational isomers *Ia* and *Ib* against temperature exhibits a maximum at about 42·5°C (Fig. 2). In the increasing part of the curve, the reaction *Ia*→*Ib* is exothermic and the ΔH value, calculated from the linear part, is $-21{\cdot}2$ kJ mol^{-1}. In the interval 35–47°C the enthalpy is close to zero and ΔS at 42·5° is $\pm 2{\cdot}82$ J mol .

. K^{-1}. Between 50 – 70°C the reaction *Ia*→*Ib* is endothermic ($\Delta H = +15{\cdot}2$ kJ mol^{-1}, calculated from the linear part). In comparison with isomerisations of other olefins, the described dependence has a remarkable course. Thus, *e.g.* in a catalysed *cis-trans* isomerisation of dimethyl 2-butenedioate[21] in solution, the amount of the *cis*-isomer at equilibrium was about 1% at temperatures below 100°C and increased exponentially at higher temperatures (8·8% at 190°C, 17·3% at 240°C). In the case of perfluoro-2-butene[22] (Fig. 3), the amount of the *cis*-isomer steadily increased in the interval 425 – 510°C. Temperature dependence of the amount of *cis*- and *trans*-2-butenes[23] at equilibrium has a similar course as that observed for compounds *Ia* and *Ib*, however, in a tenfold temperature range (Fig. 3).

As already mentioned[24], the thermodynamic stability of configurational isomers is influenced mainly by steric interactions of substituents. Therefore, *trans*-isomers usually have a lower energy content and in such cases the proportion of the *cis*-isomer (which has a higher energy content) increases with increasing temperature, such as in the case of dimethyl 2-butenedioate[21], perfluoro-2-butene[22] and 1,2-diiodoethene[25,26] (Fig. 3). However, this approach fails with 2-butene[23] for which the proportion of the *cis*-isomer begins to decrease at temperatures higher than about 500°C. We can therefore assume that the thermodynamic stability of 1,2-disubstituted ethenes is influenced also by other factors (such as *e.g.* electronic interactions of phenyl groups in 1,2-diphenylethene[24]). In this respect, 1,2-dihalogenoethenes have an exceptional position. Thus, in the equilibrium mixture of configurational isomers of 1,2-difluoroethene[27,28], 1,2-dichloroethene[29–33], 1,2-dibromoethene[32,34–36], 1-chloro-2-fluoroethene[28], 1-bromo-2-fluoroethene[28] or 1-fluoro-

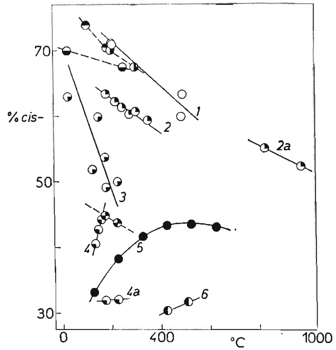


FIG. 3

Content of *cis*-Isomers in Equilibrium Mixtures in Thermal *cis-trans* Isomerisations of 1,2-Dihalogenoethenes and 2-Butene

1 CHF=CHF; *2*, *2a* CHCl=CHCl; *3* CHBr=CHBr; *4*, *4a* CHI=CHI; *5* $CH_3CH=CH-CH_3$; ◑ CHCl=CHF; ◓ CHBr=CHF; ◒ CHF=CHI; ◕ CHBr=CHI.

TABLE II

Enthalpy (Δ*H*) and Entropy (Δ*S*) Values of Thermal *cis-trans* Isomerisation of Some 1,2-Dihalogenoethenes CHX═CHY

X	Y	Temperature interval[a], °C	Equilibrium content of *cis*-isomer % rel.	Catalyst	ΔH^0 kJ mol^{-1}	ΔH_0^0 kJ mol^{-1}	ΔS^0 J mol^{-1} grad^{-1}	Ref.
F	F	204—487	71·3—63·2	I_2	3·89	—	0·561	29
		200, 300	63, 60	I_2	—	—	—	30
F	Cl	200, 300	70, 67·5	I_2	2·63[b]	—	—	30
F	Br	100, 200	74, 70	HCl	2·91[b]	—	—	30
F	I	25, 250	70, 67·4	—	0·97[b]	—	—	39
Cl	Cl	25—400	80·8—49·3	—	—	2·01	—	31
		185—275	63·4—60·3	I_2	—	2·22	—	32
		185—350	63·4—59·4	—	—	1·86	—	33
		300, 350	60·8, 59·4	—	—	—	—	34
		825, 975	55·1, 52·4	—	3·04[b]	—	1·09[b]	35
Br	Br	126·6—178·4	51·8—49·1	I_2	0·544	—0·419	2·51	36, 37
		20, 50	63, 60	HBr	—	—	—	34
		175, 225	52·7, 43·8	—	—	—	—	38[c]
Br	I	175, 225	44·8, 43·8	—	—	—	—	38[c], 40
I	I	130—159	40·5—44·2	I_2	—6·49	—8·374	10·05	27, 28
CF_3	CF_3	425—510	40·3—31·67	—	—3·42	—	2·03	24

[a] Temperature values, divided by a comma, are isolated data; [b] calculated for a linearised temperature dependence; [c] intermolecular exchange of halogens.

-2-iodoethene[37], the *cis*-isomers preponderate (*i.e.* they are thermodynamically more stable) (Table II, Fig. 3) and their proportion decreases with increasing temperature. Also *cis*-1-bromo-2-iodoethene[26,38] is more stable with increasing temperature than the *trans*-isomer. The magnitude of this so-called *cis*-effect decreases in the order 1,2-difluoroethene (the *cis*-isomer is more stable[39] by 4·52 kJ mol^{-1}), 1,2-dichloroethene and 1,2-dibromoethene (Table II). In the case of 1,2-diiodoethene[25,26], the *trans*-isomer is already thermodynamically more stable whereas for 1,2-dichlorodifluoroethene no perceptible energy difference between the isomers has been found[40].

Many authors tried to explain this *cis*-effect in halogeno compounds by resonance theory[31], carbon–halogen bond dipole repulsion[27], attractive electrostatic forces[41], dispersion forces[42] or by a complex of bonding and nonbonding interactions[28,36]. Model calculations, using the molecular orbital theory, have shown[43,44] that the interactions of lone electron pairs of halogeno substituents with each other or with a double bond can give rise to attractive forces between lone electron pairs of substituents. It followed also from the *ab initio* calculations of electronic structure of 1,2-difluoroethene[45] that the *cis*-isomer is more stable than *trans*-1,2-difluoroethene at the Hartree–Fock level theory, part of the stabilisation of the *cis*-isomer is due to steric attraction between fluorine atoms and another part of this stabilisation is due to a greater correlation energy in the *cis*-isomer. On the other hand, however, the structural evidence indicates[46] that the two fluorine atoms in the *cis*-1,2-difluoroethene repel each other[47].

In our case, it is probable that the *cis*-effect influences the temperature dependence of the equilibrium between *Ia* and *Ib* and is the cause of its unusual course (Fig. 2). The upward part of the curve corresponds to an increasing proportion of *cis*-isomer with increasing temperature, similarly as in the case of other disubstituted ethenes[21-26]. Due to the steric interactions[10] between the substituents —$COOCH_3$ and —$CF(CF_3)COOCH_3$, the *cis*-isomer *Ia* has a greater energy content. In the region 35 – 50°C this steric interaction probably begins to be outweighed by the stabilizing *cis*-effect of the fluorine atoms. At still higher temperatures, this *cis*-effect gradually prevails over the the steric interaction and thus the energy content of the *cis*-isomer grows with increasing temperature more slowly than the energy content of the *trans*-isomer; this leads to a decrease in the *cis*-isomer content. As seen from Table II and Fig. 3, the influence of the *cis*-effect persists even at high temperatures.

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