Table 3

Velocity constant for the reaction of pyridine with ethyl iodide at 60°C *

solvent	$k_{1\ atm.}$	$k_{3000\ atm.}$	$k_{3000} : k_{1\ atm.}$
Hexane	$4{,}75 \cdot 10^{-5}$	$3{,}71 \cdot 10^{-4}$	7.8
Acetone	$7{,}61 \cdot 10^{-3}$	$5{,}99 \cdot 10^{-2}$	7.9

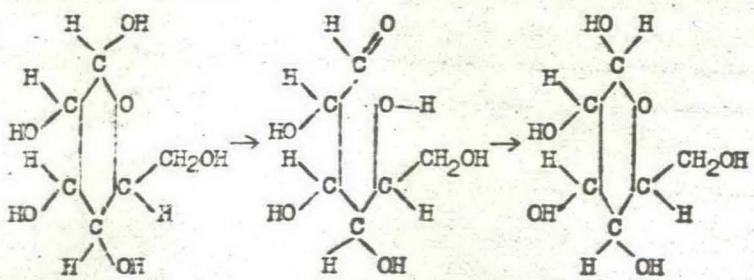
It may be mentioned that the reaction product is insoluble in hexane. Nevertheless, the change in velocity constant with pressure is exactly the same in hexane as in acetone, where the reaction product is solvated.

The data given here confirm the hypothesis that acetone molecules do not enter into the composition of the activated complex for the reaction between pyridine and ethyl iodide.

b) The Mutarotation of Glucose

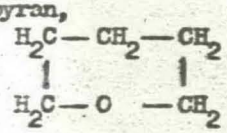
The mutarotation of glucose in aqueous solution has been studied over a wide range of pressure - up to 10,000 atmospheres [39] (see also [40]). The investigation has shown that this reaction, which is found to be unimolecular, is accelerated by pressure. Values of $\Delta V^{\neq}$, calculated by equation (III), were -9 cm^3/mole in the pressure range 1-2500 atm., -8 cm^3/mole from 2500 to 5000 atm., and 5 cm^3/mole from 5000 to 10,000 atm. Such a decrease in the average negative value of $\Delta V^{\neq}$ is quite natural if the compressibility of the substances at such high pressures is taken into account. In this connection it is known that in the reaction between pyridine and ethyl iodide, the value of $-\Delta V^{\neq}$ also falls from 16.4 cm^3/mole in the pressure range 1-3000 atm. to 8.0 cm^3/mole in the range 5000-8500 atm. [41]

At present it may be assumed, on the basis of many investigations, that the conversion of α-glucose to β-glucose (I and III, below) proceeds via an open aldehyde chain (II), i.e.



(I) (II) (III)

The question arises, which stage of this process is responsible for the increased reaction rate as the pressure rises. It has been suggested in the literature [40] that the stage in question is the formation of the aldehydic compound. On the basis of the results obtained from the investigation of the reaction under pressure, such a suggestion would lead to the result that under the experimental conditions the ring-opening would entail a diminution of the volume. In all similar cases, a decrease in volume does not occur when a ring is opened, but, on the contrary, during the cyclisation of an open chain. Thus, for example, tetrahydropyran,



is denser than n-valeraldehyde, $CH_3(CH_2)_3CHO$. In this case the difference in molar volumes is more than 7 cm^3/mole, i.e. not far from the $\Delta V^{\neq}$ for the mutarotation of glucose.

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* k is expressed in litres/mole minute^{-1}.