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V. G. VASIL' EV and E. N. KHARLAMOVA

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Abstract

Full Text

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PHYSICAL CHEMISTRY

V. G. VASIL' EV and E. N. KHARLAMOVA

INVESTIGATION OF THE STRENGTH OF C –O BONDS BY ISOTOPIC EXCHANGE

(Presented by Academician S. S. Medvedev, 4 III 1960)

The strength of C–O bonds in simple and complex ethers is of both theoretical and practical interest, since it plays a certain role in the thermal stability of polyester resins.

The authors investigated the relative strength of bonds in simple and complex ethers of various structures by the method of isotopic exchange with C¹⁴. The relative measure of strength was taken to be the fraction of exchange (as a percentage of equilibrium) attained, under the given experimental conditions, over a certain fixed period of time. The conditions were chosen so that the fraction of exchange was small and in any case did not exceed 20–40%; therefore the values of the fraction of exchange approximately corresponded to rate constants. The experiments were carried out by the ampoule method. The exchanging mixtures were equimolar; one of the components was labeled with C¹⁴ in the C*–O bond. After heating at a specified temperature, the mixture was removed from the ampoule and separated. In the first two series the fraction of exchange was determined from the radioactivity acquired by the unlabeled component (qualitatively), and in the third series from the decrease in isotope content in the labeled acid (quantitatively). The completeness of separation of the mixture was checked by a “blank” experiment carried out without heating with the same mixture, and was always entirely satisfactory.

Experimental Part

Series 1. Preliminary experiments with simple ethers. These experiments showed that *p*-nitrophenetole, *p*-chlorophenetole, *p*-diethoxybenzene, and *p*-cresol ethyl ether do not exchange with sulfur ether-C¹⁴ when heated to 300° for 20 hours (only traces of exchange were observed). Phenetole gave insignificant exchange with ether under the same conditions. Preliminary experiments on the exchange of phenetole and *p*-nitrophenetole with ethyl alcohol-C¹⁴ under

the same conditions likewise showed the absence of exchange. This indicates the strength of the C–O bond in these systems.

Series 2. Preliminary qualitative experiments on exchange in carboxyl and carbonyl compounds. The results of exchange experiments at 200° for 15 hours are given in Table 1.

Table 1

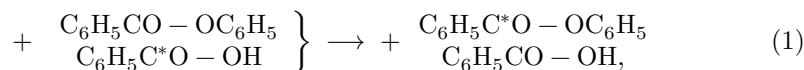
Mixture components	Exchange	Mixture components	Exchange
CH ₃ C*OOH + CH ₃ COOC ₆ H ₅	Small	(CH ₃ C*O) ₂ O + CH ₃ COOC ₆ H ₅	Small
C ₆ H ₅ C*OOH + C ₆ H ₅ COOC ₂ H ₅	None	(CH ₃ C*O) ₂ O + CH ₃ COC ₆ H ₅	None
C ₆ H ₅ C*OOH + C ₆ H ₅ COOC ₆ H ₅	Significant	(C ₆ H ₅ C*O) ₂ O + C ₆ H ₅ COOC ₆ H ₅	Small
Same, 300°	Equilibrium	(C ₆ H ₅ C*O) ₂ O + C ₆ H ₅ COC ₆ H ₅	None

As is seen from Table 1, ketones do not exchange with anhydrides; evidently, under these conditions the C–CO bond is not affected by exchange.

On the basis of these preliminary experiments, the system C₆H₅COOC₆H₅ + C₆H₅C*OOH was chosen for further quantitative experiments.

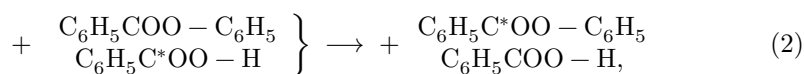
Series 3. Quantitative study of exchange in the system phenyl benzoate + benzoic acid and determination of the site of bond cleavage during exchange. Using this system as an example, the authors investigated the relative strength of the two C–O bonds in esters by the method of double isotope exchange developed by them. The principle of this method is that the exchange experiment in the given system is carried out twice under identical conditions (temperature, time, amount, etc.), but with the difference that in the first experiment the acid is labeled with C¹⁴ in the carboxyl group, and in the second it is labeled with O¹⁸ in both O atoms in the carboxyl group.

If exchange proceeds at the first C–O bond, i.e., according to scheme 1,



then it should be expected that the fraction of exchange for C¹⁴ will be twice as large as for O¹⁸.

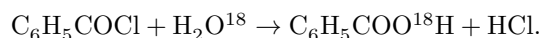
If exchange proceeds at the second C–O bond, i.e., according to scheme 2,



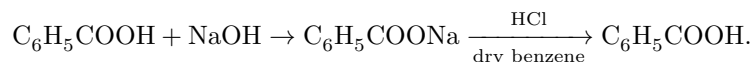
then equality of the fractions of exchange for C¹⁴ and for O¹⁸ should be expected.

Finally, when both mechanisms are present, by comparing the results of the two experiments it is possible to determine the fraction of participation of each. In this way one can determine through which of the two bonds exchange proceeds in the ester, i.e., determine their relative strength.

Benzoic acid-O¹⁸ was synthesized according to the scheme



Since the equilibrium distribution of O¹⁸ between the oxygen atoms in the carboxyl group is achieved only in the state of the benzoate ion, the synthesized benzoic acid was converted into sodium benzoate and then back into the acid:



Exchange experiments of benzoic acid-C¹⁴ and benzoic acid O¹⁸ with phenyl benzoate were carried out in parallel at $t = 200^\circ$ for 5 hours, with determination of the percentage of exchange.

Analysis of the initial benzoic acid-C¹⁴ and of the benzoic acid after exchange was carried out by wet oxidation to CO₂ according to a modified Van Slyke-Folch method.

Experimental results. The mean count of BaC¹⁴O₃ samples from benzoic acid-C¹⁴ before exchange was 733 imp/min (therefore, the decrease in activity at equilibrium exchange would be $733 : 2 = 366$ imp/min). The mean count of identical samples after exchange was 581 imp/min (therefore, the decrease in activity in the experiment was $733 - 581 = 152$ imp/min). The fraction of exchange = $\frac{152 \cdot 100}{366} = 41.5\%$.

For analysis of benzoic acid for its O¹⁸ content, it was decarboxylated, and the resulting CO₂ was analyzed for O¹⁸ content on an MI-1303 mass spectrometer*.

Experimental results. The O¹⁸ content in benzoic acid before exchange was 8.49 at.%, after exchange 7.62 at.%. The fraction of exchange is 21%.

The fraction of exchange between phenyl benzoate and benzoic acid-O¹⁸ was calculated by the formula

$$x = \frac{A - A_1}{A - \frac{A+0.22}{2}},$$

where A is the O^{18} content before exchange (at.%), A_1 is the same after exchange, and 0.22 is the natural O^{18} content in phenyl benzoate before exchange (at.%).

Comparing the fractions of exchange of phenyl benzoate with benzoic acid- C^{14} and of phenyl benzoate with benzoic acid- O^{18} , it may be considered established that the exchange between them proceeds entirely according to scheme 1, i.e., through the C–O bond located between the carboxyl carbon and the ester oxygen.

Research Physicochemical Institute
named after L. Ya. Karpov

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Note: Figure translations are in progress. See original paper for figures.

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