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**Abstract**

**Full Text**

## **Reports of the Academy of Sciences of the USSR**

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### **PHYSICAL CHEMISTRY**

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## **DETERMINATION OF RELATIVE ADSORPTION COEFFICIENTS BY THE ISOTOPE-DILUTION METHOD**

The so-called relative <sup>(1,2)</sup> adsorption coefficients have acquired great importance in studies of heterogeneous catalytic processes, especially after it was proved that they are constants entering into the kinetic equations <sup>(3,4)</sup> of a number of reactions. Recently, the possibility has been pointed out of using them to determine the magnitudes of bond energies on catalysts <sup>(5)</sup>.

In a study of the mechanism of dehydration of ethyl alcohol <sup>(6)</sup>, we carried out, on aluminum oxide, adsorption of a mixture of ethyl alcohol and ether labeled with C<sup>14</sup>, and then displaced the adsorbed products with the same mixture of unlabeled components. From these experiments, applying the isotope-dilution method, it is possible to determine the amounts of alcohol ( $\Gamma_1$ ) and ether ( $\Gamma_2$ ) adsorbed on the catalyst, which may be of interest from the standpoint of studying adsorption of mixtures. On the other hand, these quantities are evidently related to the adsorption coefficients by the simple relation

$$\frac{\Gamma_2}{\Gamma_1} = \frac{\Gamma_2^m p_2 b_2}{\Gamma_1^m p_1 b_1} = \frac{\Gamma_2^m p_2}{\Gamma_1^m p_1} z', \quad (1)$$

where  $\Gamma_1^m$  and  $\Gamma_2^m$  are the amounts of alcohol and ether required to cover the surface with a monomolecular adsorption layer;  $p_1$  and  $p_2$  are the partial pressures of alcohol and ether;  $b_1$  and  $b_2$  are the adsorption coefficients;  $z'$  is the relative adsorption coefficient. The value  $z'$ , generally speaking, may differ somewhat from that determined by the reaction-kinetic method, since in the latter case it pertains to surface sites responsible for catalysis, whereas in the former it pertains to adsorption. At high temperatures this difference should not be significant. The experiments described below may also be of interest from the standpoint of applying the isotope-dilution method to the study of adsorption of mixtures.

Our experiments were carried out in a flow apparatus. The catalyst—active aluminum oxide (granules 0.5–1 mm), in an amount of 2.8 g (5 ml)—was placed in a quartz tube, the temperature of which was maintained within the range  $120 \pm 1^\circ$ . A mixture of alcohol and ether was fed into the tube with the catalyst at a rate of 0.05 ml/min; depending on the purpose of the experiments, one or both components of the mixture were labeled with radioactive carbon. The products that were not adsorbed on the catalyst were collected in a receiver cooled to  $-50^\circ$ . The tube with the catalyst was then purged with nitrogen for 20–30 min. (Special experiments showed that under these conditions the active products are completely removed from the reactor walls.) After purging with nitrogen, the receiver was replaced, and a mixture of alcohol and ether containing no radioactive carbon was fed into the tube with the catalyst at a constant rate of 0.05 ml/min. This caused displacement of the radioactive products adsorbed on the aluminum oxide. The resulting mixture was collected in the receiver, separated by distillation on a column with a vacuum jacket, after which determinations were made.

the specific radioactivity of the alcohol and ether was determined, as described earlier <sup>(6)</sup>. Special experiments showed that the completeness of separation reached  $99.3 \pm 0.2\%$ .

First of all, it was necessary to determine whether exchange of radiocarbon occurs between the alcohol and ether under the experimental conditions. For this purpose, 1 ml of a mixture of ether and alcohol containing 94% ether and 6% (by weight) labeled alcohol, whose radioactivity was 78,000 imp/min per 1 mg of barium carbonate, was passed over the catalyst, and, after purging with nitrogen, 5.6 ml of an inactive mixture of alcohol and ether (1 : 1) was passed through. Alcohol and ether were isolated from the collected condensate, and their specific activities were determined as in <sup>(4, 6)</sup>.

Table 1

Specific radioactivity of alcohol and ether in the condensate (in imp/min per 1 mg of barium carbonate)

A			B			C			D			
No. of ex- per- i- ment	alcohol	ether	No. of ex- per- i- ment	alcohol	ether	No. of ex- per- i- ment	alcohol	ether	No. of ex- per- i- ment	alcohol	ether	
1	1520	15	3	20	0	18	115	6	18	250	380	
9	1420	18	7	15	0	19	120	6	19	260	370	
11	1560	—	8	30	0	20	117	5	20	230	370	
15	1460	—	Average 22			Average 17			6	Average 247		373
17	1590	13										
Average	1514	15										

The results of these experiments are given in Table 1A. As can be seen, the

radioactivity of the ether averages only 0.1% of the radioactivity of the alcohol, which does not exceed the possible contamination of the ether with alcohol in the separation method used by us. Thus, it may be concluded that at 120° over aluminum oxide, ether is not formed from alcohol.

It was also necessary to determine how completely the adsorbed products are displaced as a result of passing the mixture of alcohol and ether. For this purpose, after purging with nitrogen, 5.6 ml of inactive mixture was again passed through, and the radioactivity of the alcohol and ether from the condensate was determined. The results are given in Table 1B. According to this table, the radioactivity of the alcohol is only 1-2% of that obtained in Table 1A, and it follows from this that passage of the first 5.6 ml of mixture displaces the alcohol adsorbed initially sufficiently completely.

To determine the amounts of alcohol and ether adsorbed on the surface of aluminum oxide at 120°, a mixture of alcohol and ether of equal specific radioactivity (1 : 1 by weight) was prepared.

The mixture was obtained by dehydration of radioactive alcohol (2300 imp/min per 1 mg of barium carbonate) over aluminum oxide. At 120°, 1 ml of this mixture was passed over the catalyst; the receiver with condensate was disconnected, and the condensate was kept for control experiments (see below). Then nitrogen was blown through the system, and a portion of inactive mixture (5.6 ml) was again passed over the catalyst; the specific activities of the alcohol and ether collected in the receiver were determined. The results of determining the specific activities are given in Table 1C.

The data of Table 1C make it possible, by means of the isotope-dilution method, to calculate the amounts of alcohol and ether retained (chemisorbed) by the catalyst, and then, by means of equation (1), the relative adsorption coefficient of ether. The 1 ml of labeled mixture of alcohol and ether that was passed over the catalyst in the experiments of Table 1C contained 8.2 mmol of alcohol and 5.1 mmol of ether. Denoting by  $\Gamma_1$  and  $\Gamma_2$  the amounts of labeled alcohol and ether (in mmol) retained by the catalyst and then displaced by the inactive mixture; by  $N_1$  and  $N_2$ , the total amounts of alcohol and ether

(in mmoles) in the receiver after the inactive mixture had been passed through; through  $\beta_1$  and  $\beta_2$ —their specific activities, we obtain the following equalities:

$$N_1\beta_1 = \Gamma_1 \cdot 2300, \quad N_2\beta_2 = \Gamma_2 \cdot 2300,$$

whence

$$\Gamma_1 = \frac{8,2 \cdot 5,6 \cdot 117}{2300} = 2,34, \quad \Gamma_2 = \frac{5,1 \cdot 5,6 \cdot 6}{2300} = 0,075,$$

or, respectively, 0,84 and 0,027 mmole/g.

To the condensate left as a control, 5,6 ml of inactive mixture was likewise added, after which the specific activity of the alcohol and ether was determined in the resulting mixture. The results of the determination are given in Table 1Γ.

On the other hand, calculation of  $\beta'_1$  and  $\beta'_2$  from the values  $\Gamma_1$  and  $\Gamma_2$  gives

$$\beta'_1 = \frac{(8,2 - 2,34) \cdot 2300}{(8,2 \cdot 5,6) + 8,2 - 2,34} = 260 \frac{\text{imp}}{\text{min} \cdot \text{mg}}, \quad \beta'_2 = \frac{(5,1 - 0,075) \cdot 2300}{(5,1 \cdot 5,6) + 5,1 - 0,075} = 340 \frac{\text{imp}}{\text{min} \cdot \text{mg}}.$$

As can be seen, the calculated and experimentally obtained values of  $\beta'$  (Table 1Γ) agree satisfactorily with one another.

The partial pressures of alcohol and ether  $p_1$  and  $p_2$  in the methane mixture were respectively 0,62 and 0,38 atm. Then, taking the ratio  $\Gamma_1^m/\Gamma_2^m$  to be equal to the reciprocal ratio of the areas (7) occupied by the alcohol and ether molecules, we have

$$z' = \frac{\Gamma_2 \Gamma_1^m p_1}{\Gamma_1 \Gamma_2^m p_2} = \frac{0,075}{2,34} \cdot 0,8 \cdot \frac{0,62}{0,38} = 0,04.$$

In the work of Balaceanu and Yungers (8), relative adsorption coefficients of ether (with respect to alcohol) on aluminum oxide, obtained by another method, are reported for 225, 245, and 260°, equal respectively to 0,16; 0,29; and 0,4. Extrapolation of these values to 120° gives a value close to that found by us.

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

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