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Abstract

Full Text

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M. N. CHUMACHENKO and L. B. TVERDYUKOVA

MICRODETERMINATION OF ACTIVE HYDROGEN BY GAS CHROMATOGRAPHY

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For the determination of active hydrogen in organic compounds, a number of methods have been proposed, based on the interaction of organic compounds with Grignard reagent (1-8) or $LiAlH_4$ (9-11), on titration (12), and on acylation (13). In methods based on reaction with CH_3MgJ and $LiAlH_4$, the amount of methane or hydrogen evolved is determined gasometrically (1-11), manometrically (14, 15), or by isotopic analysis, using $LiAlD_4$ or $LiAlT_4$ (16, 17). Some authors have proposed burning the evolved gases and determining CO_2 and H_2O gravimetrically (18) or by titration (19). The desire to eliminate the blank experiment led to the development of methods in which the compound being analyzed, without preliminary dissolution in an indifferent solvent, reacts directly with a solution of the reagent (9, 15, 20). The instruments used in these methods are in most cases developments of the original simple apparatus of Zerevitinov and have the same shortcomings, which make the results of the analysis dependent on fluctuations in temperature and pressure.

Fig. 1. Schematic diagram of the apparatus. *1* –cylinder with carrier gas; *2* –low-pressure reducer; *3* –control valve of the comparison chamber; *4* –coil; *5* –detector; *6* –cylinder with control gas; *7* –four-way actuator; *8* –membrane flow switch; *9* –reaction system; *10* –thermostat; *11* –EPP-09 electronic potentiometer.

We have for the first time developed a micromethod for determining active hydrogen in organic compounds, with chromatographic determination of the amount of gas evolved as a result of the reaction of the substance with a solution of $LiAlH_4$ in tetrahydrofuran. The choice of the chromatographic method was dictated by the necessity of separating hydrogen and solvent vapors on the recording diagram and by the particular features of carrying out the reaction. This method makes it possible to obtain accurate results and to reduce the time of a single determination to 5-7 min. The accuracy of our method is ensured by the high sensitivity of the detector, whose operation is based on measuring the

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

heat capacity of gases, which excludes the influence of temperature and pressure fluctuations on the results of the analysis; by the large difference between the heat capacities of hydrogen and nitrogen, which serves as the carrier gas; and by the elimination of the blank experiment (reac-

tion is carried out directly with the reagent solution, without preliminary dissolution of the weighed sample of the substance; the amount of hydrogen is determined graphically from a calibration curve constructed using a known substance under the conditions of the analysis).

We constructed an apparatus (Fig. 1) consisting of a reaction system and a chromatograph,* equipped with a special device; the latter makes it possible to carry out the reaction directly in the chromatograph system and to direct all gaseous reaction products into the detector. This is accomplished by means of a membrane flow switch, which consists of four disks with corresponding channels and three rubber membranes. The membrane switch is controlled by a four-valve actuating mechanism. Depending on the position of the membranes, the carrier gas enters either directly into the detector working chamber or first passes through the reaction flask. Of all the reaction systems we tested, the most suitable proved to be the system shown in Fig. 2. The reaction flask, having capillary outlets at the same level, is small in volume, has no "dead" spaces, and is rapidly and thoroughly flushed by the carrier-gas stream. The funnel is connected to the flask by means of a ground-glass stopper. The remaining reagent serves as the seal. Dry nitrogen is used as the carrier gas; its flow rate (55–60 ml/min) is maintained strictly constant by means of a regulating valve.

Fig. 2

Fig. 3

Studies showed that the most suitable chromatographic column for our purposes is a metal coil 2 m long and 5 mm in internal diameter, packed with activated BAU-2 charcoal and placed in a thermostat with distilled water at room temperature; the best solvent, apparently, is absolute tetrahydrofuran, owing to its chemical inertness combined with high dissolving power, although in each specific case a more suitable solvent may be selected for the substance being analyzed from among those in which $LiAlH_4$ dissolves sufficiently well. A solution of $LiAlH_4$ in tetrahydrofuran is prepared by shaking 3 g of finely ground $LiAlH_4$ in 100 ml of absolute tetrahydrofuran, followed by decantation. Owing to careful selection of the entire set of determination conditions, the peaks ob-

Fig. 4

Figure 4: Fig. 4

tained on the recording diagram have a symmetrical shape (Fig. 3). This makes it possible to calculate their area by the ordinary formula for determining the area of triangles.

Fig. 4

To construct the calibration curve, distilled 8-hydroxyquinoline was used as the standard substance; weighed portions of 8-hydroxyquinoline were taken within the range 1.187–16.001 mg. Thirty points were obtained, through which the calibration curve shown in Fig. 4 was drawn.

* The chromatograph was designed by engineer F. G. Leenson.

Table 1

No.	Name of substance and gross formula	Sample weight, mg	Peak area, mm^2	Active hydrogen content, %, found	Active hydrogen content, %, calculated	Δ
1	Methyl ether of Δ^1,3,5(10),8-18-nor-*D*-homoestratetraendiol-3,15-*β*-one-17*α* $C_{19}H_{22}O_3$	6.2894.897	119101	0.320.35	0.34	−0.02+0.01
2	Methyl ether of Δ^1,3,5(10),8-*D*-homoestratetraendiol-3,14-*ξ*-one-17*α* $C_{20}H_{24}O_3$	5.7603.540	11170	0.320.33	0.32	0.00+0.01

No.	Name of substance and gross formula	Sample weight, mg	Peak area, mm^2	Active hydrogen content, %, found	Active hydrogen content, %, calculated	Δ
3	19-Nor-17$\alpha\beta$-ethyl-*D*-homotestosterone$C_{21}H_{32}O_2$	3.6743.212	6864	0.320.33	0.32	0.00+0.01
4	Methyl ether of Δ^1,3,5(10),8-17$\alpha\alpha$-methyl-*D*-homoestratetraendiol-3,17$\alpha\beta$$C_{21}H_{28}O_2$	3.1533.260	6366	0.330.34	0.33	0.00+0.01
5	Methyl ether of Δ^1,3,5(10),8,14-*D*-homoestrapentaendiol-3,17$\alpha\beta$$C_{20}H_{23}O_2$	5.3251.040	11622	0.360.35	0.34	+0.02+0.01
6	Δ^4,9-19-Nor-*D*-homoandrostadienol-14ξ-3,17α-dione$C_{19}H_{24}O_3$	4.9292.645	14073	0.470.47	0.44	+0.03+0.03

No.	Name of substance and gross formula	Sample weight, mg	Peak area, mm^2	Active hydrogen content, %, found	Active hydrogen content, %, calculated	Δ
7	Ethylene ketal, syn, cis-Δ^9(14)-dodecahydrophenanthrenediol-1α, 4α-one-7 $C_{14}H_{20}O_4$	2.7522.890	134142	0.810.81	0.80	+0.01+0.01
8	threo-β-(cis-2-oxicyclohexyl)-β-dimethylaminoethanol $C_{10}H_{21}O_2N$	1.8011.910	116120	1.051.07	1.07	−0.020.00
9	threo-β-(trans-2-oxicyclohexyl)-β-dimethylaminoethanol $C_{10}H_{21}O_2N$	1.4451.753	89113	1.041.07	1.07	−0.030.00
10	Benzoic acid $C_7H_6O_2$	1.0202.238	51109	0.830.81	0.83	0.00−0.02
11	N-trifluoroacetylbenzylamine $C_9H_6ONF_3$	4.0904.606	123146	0.500.53	0.50	0.00+0.03
12	2,5-Diphenylpyrrozolinone-2 $C_{15}H_{12}ON_2$	4.0756.014	102155	0.420.43	0.43	−0.010.00

Using the method developed, we analyzed a number of substances; satisfactory results were obtained for all of them, some of which are given in Table 1. A detailed procedure will be published in the *Journal of Analytical Chemistry*.

Institute of Chemistry of Natural Compounds
Academy of Sciences of the USSR

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