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Abstract

Full Text

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ON THE ISOTOPIC ANALYSIS OF NITROGEN

BY THE METHOD OF ELECTRON PARAMAGNETIC RESONANCE

Recently, the method of electron paramagnetic resonance (e.p.r.) has been successfully applied to measuring the concentration of free radicals and paramagnetic particles.

In the present work, the possibility was studied of using this method for quantitative analysis of the nitrogen isotopes N^{14} and N^{15} in organic and inorganic compounds. The application of the e.p.r. method for this purpose is based on the study of the hyperfine nuclear structure of the spectra of free radicals containing N^{14} and N^{15}. Since the magnetic moments of the nuclei N^{14} and N^{15} are respectively equal to 1 and 1/2, then, in the interaction of the spins of the unpaired electron and the nitrogen nucleus, one should expect the appearance in the e.p.r. spectrum of three lines for N^{14} and two lines for N^{15}.

This circumstance can be used for purposes of analysis provided a number of conditions are fulfilled: 1. It is necessary to have a stable nitrogen radical with good splitting of the singlet on nitrogen. The lines of the triplet and doublet in the e.p.r. spectrum must not overlap one another. 2. The nitrogen of chemical compounds must be converted into a stable radical by a general simple method and without a noticeable isotope effect. 3. It is desirable that the free radical be stable in solutions in air for a sufficiently long time.

Fig. 1. E.p.r. spectrum of radical I

These conditions are satisfied by the free radical obtained by us, to which the structure 2,2,6,6-tetramethyl-*N*-dehydropiperidone-4-oxide-1 (I) can be assigned. Radical I is formed upon oxidation of triacetonamine with sodium perwolframate in an aqueous medium. Triacetonamine is readily obtained by the interaction of ammonia with phorone:

Fig. 2. EPR spectrum of radical I labeled with N15 at 28%

Figure 2: Fig. 2. EPR spectrum of radical I labeled with N15 at 28%

$$\text{triacetonamine formation scheme} \quad \longrightarrow \quad \text{radical I} \tag{I}$$

The nitrogen of the compounds being analyzed is converted into ammonia by conventional methods. The time required for synthesis of the radical is 40 min. An aqueous solution of the radical is stable in air for several weeks.

Spectrum I consists of three lines of relative intensity $1:1:1$ with a separation between the centers of the lines of 15.7 Oe (Fig. 1). We prepared solutions of samples of radical I with an N^{15} content from 3.2 to 28%. In this case, in the EPR spectrum, in addition to the triplet, two lines appear corresponding to the interaction of the unpaired electron with the N^{15} nucleus. The hyperfine structure of the spectrum is well resolved in air in dilute aqueous, aqueous-alcoholic, and ether solutions at room temperature (Fig. 2).

At an N^{15} content below 2%, the EPR spectrum is resolved considerably less readily. The separation between the doublet lines is 21.9 Oe. The center of the EPR spectrum of radical I is shifted upfield relative to the center of the spectrum of 1,1-diphenyl-2-picrylhydrazyl by 2.9 Oe.

Consideration of the spectra obtained makes it possible to conclude that they are suitable for determining the relative content of N^{14} and N^{15}. The determination can be carried out in the usual way by calculating the areas occupied by the doublet and triplet parts of the spectrum. Since the method under consideration is based on a single measurement without comparison with a standard, there is no need to take into account a number of factors that reduce the accuracy of the analysis (1). During measurements, conditions may arise under which it will be difficult to obtain good resolution of the spectra. For example, when working with insufficiently dilute solutions of radical I (which may be required in order to obtain a satisfactory excess of the signal over the background), the hyperfine structure of the spectrum is partially smeared (Fig. 3a, b). In this case an approximate calculation should be made without taking into account peaks 2, 3, 8, and 9, according to the formula

Fig. 2. EPR spectrum of radical I labeled with N^{15} at 28%

$$N^{15} = \frac{a_4 + a_7}{a_4 + a_7 + a_1 + a_{10} + 0.5a_5 + 0.5a_6} \cdot 100\ (\%),$$

where a denotes the area or height of a peak.

When the values of the areas were substituted into this formula for samples containing 28.0, 25.2, and 19.8% N^{15}, the following values were found, respectively: 27.9, 25.0, and 18.9%.

Table 1

Results of isotope analysis

No.	Taken, %	Found, % without correction	Found, % after correction	No.	Taken, %	Found, % without correction	Found, % after correction
1	3.2	3.6	4.9	6	17.0	15.6	16.3
2	5.9	5.2	6.4	7	19.8	18.8	19.3
3	8.7	7.2	8.3	8	22.5	22.9	23.2
4	11.4	9.5	10.5	9	25.2	24.8	25.2
5	14.2	13.3	14.1	10	28.0*	28.3	28.4

Note. Nos. 1-9 are the mean of 4 measurements. No. 10 is the mean of 15 measurements.

* The N^{15} content in the sample was determined mass-spectrometrically. The other samples were obtained by dilution of sample No. 10 with unlabeled ammonium nitrate.

The results of the analysis obtained when the values of peak heights were substituted into the indicated formula are given in Table 1. More accurate results in this case are obtained if one uses the correlation dependence between the composition taken (x) and that obtained (y) (2). For our experiments this dependence

had the form $y = 1.05 \cdot x - 1.51$. The residual variance for a single measurement was $\sigma = 1.16$. The limits within which 95% of all values obtained in the case of three measurements lie are $\pm 1.4\%$ (absolute), measured from the regression line.

Experimental Part

The study of EPR spectra was carried out in aqueous-alcoholic media in air at room temperature on a direct-amplification spectrometer with double modulation of the magnetic field and an operating frequency of $\sim$ 9000 MHz of the EPA type. The spectra were recorded as first derivatives of the absorption line on an EPP-09 recorder. Part of the measurements was repeated on an EPR-2 spectrometer (^{3}), with the kind assistance of A. L. Buchachenko.

Fig. 3. EPR spectra of radical I at insufficient resolution; right—N^{15} content 28%; left—N^{15} content 14.2%.

The preparation of radical I was carried out as follows. To 1 ml of an aqueous solution containing 0.2 mmol of ammonium nitrate, 0.02 ml of a 25% alcoholic

Fig. 3. EPR spectra of radical I at insufficient resolution; right—N^{15} content 28%; left—N^{15} content 14.2%

Figure 3: Fig. 3. EPR spectra of radical I at insufficient resolution; right—N^{15} content 28%; left—N^{15} content 14.2%

solution of foron, 0.4 ml of 0.5 *N* NaOH, and 0.5 ml of C_2H_5OH were added. The mixture was heated at 100° in a sealed ampoule for 15 min. After this, 0.2–1 mg of Trilon B, 0.2 ml of 30% hydrogen peroxide, and 0.1 ml of a 1 *M* solution of sodium tungstate were added to the contents. The mixture was heated at 50° for 15 min. About 0.01 ml of the resulting radical solution was taken for recording the spectra. Changing the concentration of the ammonium salt during synthesis of the radical by a factor of 10 does not affect the accuracy of the determination. By the proposed method, nitrogen-containing compounds in amounts down to 0.02 mg can be analyzed.

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