SULFUR ISOTOPE EFFECT IN THE PHOTOLYSIS OF SO_2

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UDC 539.183.2:541.7:546.224-31

Significant photolytic separation of the sulfur isotopes was noted upon the irradiation of gaseous SO_2 using a PRK-4 mercury lamp (λ 1849 Å) and the residual SO_2 was enriched in the light isotopes (Table 1). Analysis of the photolysis products indicated that the dissociation proceeds as follows:

$$3SO_2 + h\nu \rightarrow 2SO_3^* + S \qquad (1)$$

and virtually only residual SO_2 is present in the gas phase (as determined relative to the pressure change in the reaction vessel), while the vessel surface is coated with elemental sulfur and $(SO_3)_2$-type polymer compounds. The mass spectral isotope analysis carried out according to our procedure [1] with an error of ±0.2% are given in Table 1 (the initial SO_2 pressure in the vessel was 80 torr).

The sulfur isotope partition coefficient α in this process was calculated using the generally accepted expression for enrichment upon Rayleigh exhaustion. The direction of the observed isotope effect is probably a consequence of isotope exchange between the reagent and products of reaction (1), which occurs upon the interaction of SO_2 with a light quantum. Comparison of the ratios of the β-factors of these compounds and α_{av} 0.9835 may indicate that the isotope effect is a function of the isotope equilibrium constant between excited SO_3^* and SO_2. We should also note that there is a mass-dependent sulfur isotope separation, which obeys the isotope pleiad rule $\delta^{33}S \approx 0.505\ \delta^{34}S$.

TABLE 1

p, mm Hg	δ^{33} S, ‰	δ^{34} S, ‰	α	$\alpha_{av.}$
20	−11,0	−21,7	0,9827	0,9835±0,0008
1	−37,7	−74,5	0,9844	

LITERATURE CITED

1. V. I. Ustinov and V. A. Grinenko, Precision Mass Spectrometric Methods for the Determination of the Sulfur Isotope Composition [in Russian], Izd. Nauka, Moscow (1965).

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 0568-5230/88/3705- 1052$12.50