Non-exchange of Sulfur Atoms between Sulfate and Sulfonate Ions

By Mitsuo MURAMATSU

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Many works have been undertaken to determine whether the sulfur atoms in an organic molecule can exchange themselves with those in a molecule of another compound[1]. According to the reports published up to the present, a measurable rate was observed in the exchange reactions between alkyl disulfides and trisulfides[2], elementary sulfur and organic substances containing S-S or C=S bond[3], sulfite and alkylthiosulfates[4], and alkylpolysulfides and alkylmercaptides[5]. These facts may be explained by the easiness of opening and subsequent closing of sulfur bond in organic compounds. However, no exchange seemed to be reported between other sulfur-containing compounds[1].

In order to obtain further information regarding the lability of sulfur bond and to study the possibility of introducing radioactive sulfur atoms into the molecules of organic compounds, the present author has attempted to study the exchangeability of sulfur atom in sulfate with that in sulfanilate, naphthionate, β-naphthalenesulfonate, *o*-nitrophenolsulfonate, *o*-carboxybenzenesulfonate, *m*-nitrobenzenesulfonate and taurine.

Experimental

Sodium salts of taurine, sulfanilic acid and naphthionic acid were of reagent grade. Ammonium *o*-carboxybenzenesulfonate, sodium *m*-nitrobenzenesulfonate, *o*-nitrophenolsulfonate and β-naphthalenesulfonate were synthesized. All these sulfonates were recrystallized repeatedly and were dissolved to make a stock solution of 0.25 M. The solution of radioactive sulfate having specific activity of 10 mC/mol. was prepared by dissolving purified sodium sulfate into a solution of carrier-free $^{35}SO_4^{2-}$, to make a solution of 0.25 M.

Four cc. portions of sulfonate and sulfate solutions were transferred into a measuring flask and made up exactly to 10 cc. and to a desired acidity with distilled water and dilute hydrochloric acid or aqueous ammonia. The reaction mixture was then transferred into a reaction flask to which a reflux condenser was attached and was kept at desired temperature.

After the supposed exchange reaction, inorganic sulfate was separated as barium salt and the specific activity of the precipitate and the remaining sulfonate in the filtrate was determined separately after purification. In the case of naphthionate, another method of separation was also adopted; hydrochloric acid was added to the reaction mixture and the specific activity of naphthionic acid formed was determined.

TABLE I

FRACTION EXCHANGE, *F*, IN THE REACTION OF SODIUM SULFATE AND SODIUM NAPHTHIONATE: CONCENTRATION OF SODIUM SULFATE AND NAPHTHIONATE ARE BOTH 1/10 mol./l. pH=7

Time	Room temperature		91±2°C	
	F, %	Method of separation	*F*, %	Method of separation
1 hr.	0.1±0.1	$BaSO_4$		
2 〃			3.8±0·8	$BaSO_4$
4 〃	0.2±0.1	$BaSO_4$		
9 〃			−2.9±2.0	$BaSO_4$
12 〃			0.5±1.1	$BaSO_4$
21 〃	0.0±0.1	naphthionic acid		
28 〃	0.0±0.1	naphthionic acid	0.1±0.2	naphthionic acid
22 days	0.0±0.2	$BaSO_4$		
150 〃	0.1±0.8	naphthionic acid		
161 〃	0.6±0.6	$BaSO_4$		

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1) G. Hevesy, "Radioactive Indicators" (1948), Interscience Publ., Inc., New York, p. 85; A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry", (1951), John Wiley and Sons, Inc., New York, p. 346.

2) E. N. Gur'yanova and V. N. Vasil'eva, *Zhur. Fiz. Khim.*, **28**, 60 (1954).

3) E. N. Gur'yanova, ibid., **28**, 60 (1954).

4) A. Fava and G. Pajaro, *J. Am. Chem. Soc.*, **78**, 5203 (1956).

5) A. Fava and A. Illiceto, *Ricerca Sci.*, **23**, 839 (1954); S. Ikeda, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **79**, 103 (1958).

Radioactivity of each sample was measured by means of an end-window type GM counter. The quantity of the sample to be counted was little enough to ignore the self absorption of soft β-ray of sulfur-35.

Results and Discussion

It was observed that no measurable exchange of sulfur took place between sulfate and any organic sulfonates during a few decades of hours at temperature up to 91±2°C or during six months at room temperature. This was indeed the case at any pH from 2 to 10. Separation-induced exchange did not take place for any compounds studied, irrespective of the method of separation. Typical examples are shown in Table I.

Such a difficulty of exchange may be ascribed to the firm C–S bond in the sulfonate ion, rather than the S=O bond in the sulfate. Actually, a slow rate of exchange of the oxygen atom in the reaction of sulfate ion with $H_2{}^{18}O$[6] is not sufficient to explain the present results. Such a conclusion is in accord with what is familiar in organic chemistry.

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Department of Chemistry
Faculty of Science
Tokyo Metropolitan University
Setagaya-ku, Tokyo

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[6] T. C. Hoering and J. W. Kennedy, *J. Am. Chem. Soc.*, **79**, 56 (1957); T. Titani and K. Goto, This Bulletin, **14**, 77 (1939), etc.