

Preparation of ^{35}S -labelled xanthates and ^{35}S -labelled carbon disulphide by exchange reactions*

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SUMMARY

The order of the exchange reaction between potassium ethyl xanthate and elemental sulphur was determined. A mixture of ethanol and toluene was used as the solvent for the routine preparation of ^{35}S -labelled ethyl, n-butyl, n-hexyl and n-octyl xanthates at a temperature of 20° C. The dependence of the exchange rate on the presence of water was observed. The decomposition of ^{35}S -labelled ethyl xanthate in dilute hydrochloric acid was used for the preparation of labelled carbon disulphide.

INTRODUCTION.

Several papers have dealt with the preparation of various xanthates. The direct synthesis from ^{35}S -labelled carbon disulphide and alcoholic solution of potassium hydroxide has been used most frequently up to date ^(1,2). The exchange reaction between elemental sulphur and potassium ethyl xanthate has also been described, although not for preparative purposes. The exchange reaction was employed in our work for the preparation of labelled xanthates, in order to reduce the labelling cost.

Direct synthesis from the elements ^(1,4), the reaction of ^{35}S -labelled phosphorus pentasulphide with carbon tetrachloride ⁽⁵⁾, as well as exchange reactions ^(6,9) have been reported for the preparation of ^{35}S -labelled carbon disulphide. The exchange between carbon disulphide and ^{35}S -sulphide in alkaline aqueous solution proceeds at room temperature ^(6,7), while the exchange between ^{35}S -elemental sulphur dissolved directly in carbon disulphide requires temperatures higher than 200° C ^(8,9); the exchange rate at 120° C is negligible ^(10,11). Carbon disulphide is released from xanthate, when acidified.

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Because of the easy preparation of the ^{35}S -labelled potassium xanthate, we regard the decomposition of this substance as a suitable method for the preparation of ^{35}S -labelled carbon disulphide.

EXPERIMENTAL PART.

The potassium ethyl, *n*-butyl, *n*-hexyl and *n*-octyl xanthates were prepared at room temperature from the solutions of the corresponding alcoholates and carbon disulphide; in all cases an excess of dry ether was added to complete crystallization. Iodometric determination provided 101,2 and 100,9 per cent of theory for ethyl and *n*-butyl xanthates respectively.

The solution of radioactive elemental sulphur was prepared by dissolving sulphur of high specific activity (2-5 mC per mg) in dry toluene. The solution of non radioactive sulphur in dry toluene contained 10 mg of sulphur per ml.

Procedure of the exchange experiments.

A volume of the radioactive elemental sulphur solution corresponding to 2 mC of ^{35}S was mixed with the necessary amount of non radioactive sulphur solution and dry toluene was added to make the total volume 13 ml. The weighed amount of potassium xanthate was dissolved in 13 ml of alcohol. The exchange was started by mixing these solutions, after they had reached the required temperature. To stop the exchange reaction, 2.5 ml aliquots were pipetted into 20 ml of dry ethyl ether; the crystalline xanthate formed immediately. The xanthate crystals were filtered off, washed with dry ether and dried in vacuo over phosphorus pentoxide.

Recommended procedure for the preparation of ^{35}S -labelled potassium xanthates.

The required quantity of potassium xanthate (50-250 mg) is dissolved in 0.05-0.2 ml of water and 2-4 ml of absolute ethanol are added. The calculated amount of highly active sulphur (up to 20 mg) is dissolved in 2-4 ml of dry toluene. The final volumes of both solvents have to be equal. The solutions are mixed and after one hour dry ether is added in excess, until crystals are formed (30-50 ml). After ten minutes the crystalline product is filtered off, washed with dry ether and dried in vacuo at room temperature.

Recommended procedures for the preparation of ^{35}S -labelled carbon disulphide.

A) ^{35}S -labelled potassium ethyl xanthate (50-200 mg) is dissolved in 5 ml of water, 5 ml pentane and 3 ml of dilute hydrochloric acid (1:3) are added successively. The mixture is thoroughly shaken and then the pentane containing the ^{35}S -carbon disulphide is distilled off. After cooling, additional 5 ml of pentane are added and distilled off. The collected pentane fractions are dried with anhydrous sodium sulphate.

B) ^{35}S -labelled potassium ethyl xanthate (approximately 2 grams) is dissolved in 10 ml of water and 10 ml of cooled hydrochloric acid are added. The crude carbon disulphide which settled down in a few minutes is transferred with minimum water into the microdistillation apparatus and distilled.

Radioactivity measurement.

A weighed amount of ^{35}S -labelled potassium xanthate (2-10 mg) was dissolved in 4 ml of 0.5 N solution of sodium hydroxide and 3 ml of 30 per cent hydrogen peroxide were added. The mixture was carefully heated until oxidation started. After completion of the oxidation excess hydrogen peroxide was destroyed by boiling the solution on a sand bath. The solution was diluted to the desired volume and 5 ml aliquots were counted on glass planchets (4 cm in diameter) under a thin-window G-M tube (Frieeseke-Hoepfner, FHZ 15a, mica 1.10 mg per cm^2). The counting device was calibrated using a standard ^{35}S solution.

An aliquot of the pentane layer containing ^{35}S -labelled carbon disulphide (or carbon disulphide directly) was added to 1 ml of ethanolic solution of sodium hydroxide. After 10 minutes, 4 ml of 0.5 N solution of sodium hydroxide and 3 ml of 30 per cent hydrogen peroxide were added and the mixture was treated in the same way as described for the labelled xanthates.

An aliquot of the toluene solution of radioactive sulphur was evaporated to dryness, and bromine followed by concentrated nitric acid were added. The mixture was carefully heated for 10 minutes, then bromine was evaporated and the solution was diluted with water to the desired volume and counted as described for the labelled xanthates.

Chemical analyses.

The xanthates were determined by iodometric titration ⁽¹²⁾. Carbon disulphide was converted to ethyl xanthate and determined in the same manner ⁽¹³⁾.

Radiochemical purity.

Xanthate was dissolved in ethanol and a droplet of this solution was transferred to chromatographic paper (Whatman N^o 4,20 \times 400 mm). *n*-Butanol saturated with 2 percent aqueous solution of potassium hydroxide was used as the solvent for ascending chromatography ⁽¹⁴⁾. The activity was measured in 1 cm strips. The paper was then sprayed with the Grote reagent to detect the spots.

RESULTS AND DISCUSSION.

To determine the order of the reaction, the exchange rate ⁽¹⁵⁾ R was estimated for solutions having different ratios of ethyl xanthate and sulphur concentrations. The experiments were carried out at 22^o C, using 96 per cent

ethanol as the solvent for ethyl xanthate. The saturation specific activity of ethyl xanthate corresponded to two exchangeable atoms in the molecule. The plots of $\log(1-F)$ against time (where F is the fraction of exchange) yielded straight lines, within the experimental error. The method of least squares was applied, and the lines extrapolated to zero time showed an apparent zero-time exchange for approximately 15-20 per cent. The exchange rates were calculated assuming the two sulphur atoms in ethyl xanthate to be chemically equivalent. The results are given in Table I.

TABLE I. Results of exchange experiments for ethyl xanthate (22° C)

[A]	[B]	$T_{1/2}$ (sec)	$R \times 10^5$	$k \times 10^2$
0.154	0.154	120	44.5	1.88
0.154	0.0770	162	22.0	1.86
0.154	0.0385	204	10.4	1.75
0.154	0.0192	228	5.19	1.76
0.0770	0.0385	284	6.26	2.11
0.0385	0.0385	432	3.09	2.09
0.308	0.0385	144	16.5	1.39

$T_{1/2}$ denotes the estimated half-time of exchange; for other symbols see the text.

The exchange rate R may be represented by

$$R = k \cdot [A]^n \cdot [B]^m,$$

where k denotes the velocity constant ($\text{litre} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$), $[A]$ and $[B]$ are the concentrations of sulphur atoms in the form of xanthate and sulphur, respectively, n and m are the orders of the reaction with respect to A and B . When $\log R$ was plotted against $\log [A]$ at constant $[B]$ and vice versa, the values of 0.88 and 1.04 were obtained for n and m , respectively. The mean value of k was $(1.83 \pm 0.09) \times 10^{-2} \text{ litre} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$.

All above mentioned experiments were carried out at 22° C. At this temperature the exchange rate was too high to resolve the first stages of exchange. Some experiments were therefore performed at 0° C. However, the plot of $\log(1-F)$ against time was found to be nonlinear (Fig. 1).

The observed non linearity of the curves is not caused by the incomplete separation⁽¹⁵⁾. It might be explained by the rather improbable assumption of the non-equivalence of the sulphur atoms in the xanthate molecule. No further experiments were made to clarify this problem, as the purpose of this work was predominantly preparative.

A dependence of the exchange rate on the presence of water was observed. As examples, the results of exchange experiments carried out using 96 per cent

ethanol and absolute ethanol as solvents for ethyl xanthate, are presented in figure 1. Even a small content of water accelerates the exchange reaction, as previously reported for dithiocarbamates ⁽¹⁶⁾.

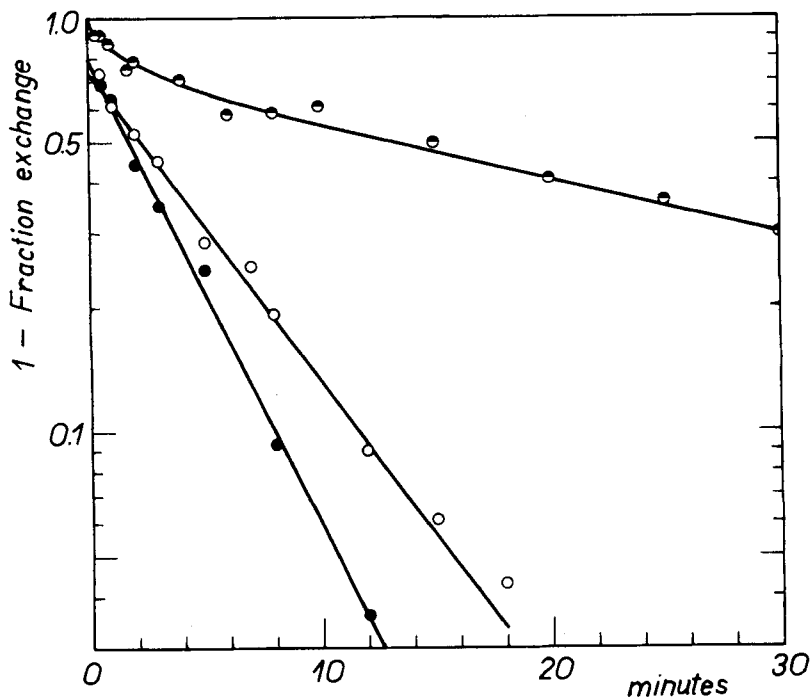


FIG. 1. — Exchange curves for ethyl xanthate-sulphur mixtures.

Solvents and temperatures : ○ absolute ethanol-toluene, 22° C; ● 96 per cent ethanol-toluene, 0° C; ● 96 per cent ethanol-toluene, 22° C. In all cases the xanthate and sulphur concentrations were 0.077 M.

The exchange experiments were also carried out with other xanthates. Complete exchange was reached for all xanthates investigated within one hour at room temperature and the saturation specific activity corresponded to two exchangeable atoms in the molecule. Ethanol may be used as the solvent for all xanthates. The experiments were performed in order to ascertain whether transesterification takes place. The radiochemical purity of the butyl xanthates exchanged in ethanol-toluene and in butanol-toluene mixture was determined. In the first case less than 1 per cent of the activity was found on the spot with R_F corresponding to ethyl xanthate. Radiochemical purity was very low in the second case; several peaks were observed between the butyl xanthate and elemental sulphur peaks. Ethanol can therefore be recommended as the solvent.

This procedure has been applied in the routine production of various xanthates for the last two years. Chemical yields of 60-70 per cent and of 50-60 percent have been attained for ethyl and butyl xanthate respectively. The activity yields depend on the xanthate-sulphur ratio and came close to the chemical yield, when small amounts of highly active sulphur were used. The specific activities of the product were in the range of 110-140 mC per gram. The activity in the form of elemental sulphur depended on the sulphur concentration and was lower than 3 per cent, if sulphur with high specific activity was used.

The preparation of ^{35}S -labelled carbon disulphide proved to be very simple. The dilution of labelled carbon disulphide with pentane may be recommended for the preparation of small quantities of product, since the losses are lower (Procedure A). The water-pentane mixture should be thoroughly shaken before distillation in order to prevent carbon disulphide from settling. The chemical yield of carbon disulphide from ethyl xanthate was 85-94 per cent, and the total activity yield from the sulphur put in is 50-65 per cent. For routine production procedure B was used. Thorough cooling with an acetone-dry ice mixture is necessary to obtain 90 per cent yield of ethyl xanthate decomposition. As the activity yield of the ethyl xanthate preparation was 85-90 per cent under these conditions, the total activity yields of the labelled carbon disulphide preparation was 70-80 per cent.

REFERENCES

1. SATO, T. — *Nippon Kagaku Zasshi*, **81** : 1338 (1960); *Chem. Abstr.*, **56** : 318c (1962).
2. SON-LIN WU. — *Hua Hseuh Tung Pao*, **1** : 58 (1963); *Nucl. Sci. Abstr.*, **18** : 3829 (1964).
3. FOKA, M. N. and BURKSER, L. E. — *Dokl. Akad. Nauk SSSR*, **99** : 1011 (1954).
4. BÜSING, K. H., SONNENSCHNEIN, W., BECHER, E. W. and DREIHELLER, H. — *Z. Naturforsch.*, **8b** : 495 (1953).
5. MARKOVA, JU. V., POZHARSKAYA, A. M., MAIMIND, V. I., ZHUKOVA, T. F., KOSOLAPOVA, N. A. and SHCHUKINA, M. N. — *Dokl. Akad. Nauk SSSR*, **91** : 1129 (1963).
6. EDWARDS R. R., NESBETT, F. B. and SOLOMON, A. K. — *J. Amer. Chem. Soc.*, **70** : 1670 (1948).
7. MARTIN, D. and VENKER, P. — *Naturwissenschaften*, **49** : 256 (1962).
8. SOKOLOV, V. A. — *Trudy vsesoyuz. nauch. tekh. konf. prim. rad. izotopov*. Moskva 1955. Izdat. ANSSSR (1958). Izotopy i izluch. v chim., 367.
9. ZEL'VENSII, Ja. D, SHALYGIN, V. A. and VANTYSH, A. N. — *Radiokhimiya*, **1** : 683 (1959).
10. COOLEY, R. A., YOST, M. D. and McMILLAN, E. — *J. Amer. Chem. Soc.*, **61** : 2970 (1939).
11. DOUGLAS, D. L., COOLEY, R. A. and YOST, M. D. — *J. Amer. Chem. Soc.*, **71** : 3237 (1949).
12. LINCH, A. L. — *Analyt. Chem.*, **23** : 294 (1951).
13. MATUZSAK, M. P. — *Ind. Eng. Chem. Anal. Ed.*, **4** : 98 (1932).
14. KARIYOHE, T., HASHIMOTO, Y. and KIMURA, M. — *Nature*, **168** : 511 (1951).
15. MYERS, O. E. and PRESTWOOD, R. J. — *Isotopic Exchange Reactions. In Radioactivity, Applied to Chemistry* (Wahl A. C., Bonner N. A., Editors). John Wiley and Sons, Inc., New York 1951, 6-43.
16. GURYANOVA, E. N. and KUZINA, L. S. — *Zh. fiz. chim.*, **32** : 2301 (1958).