

OSCILLOPOLAROGRAPHIC EXAMINATION OF SOME ORTHOSILICIC ACID DERIVATIVES II

DETERMINATION OF THE RATE OF HYDROLYSIS
PRELIMINARY PUBLICATION

By

T. DAMOKOS

Department for Inorganic Chemistry, Polytechnical University, Budapest

(Received July 28, 1962)

Presented by Prof. Dr. J. PROSZT

The number of papers published on the rate of hydrolysis of silane derivatives is relatively few; REUTHER [1], and later SHAFFER and FLANIGEN [2], [3] published results obtained by the conductometric method. Owing to the fact that — as it has been described in the first paper of this series [4], [5] — the concentration of alkoxy-silanes and substituted alkoxy-silane derivatives can readily be estimated by the oscillopolarographic method, while at the same time the products of hydrolysis are oscillopolarographically inactive, an attempt was made to determine the rate of hydrolysis of alkoxy-silane derivatives by this technique. Similar tests made with other compounds (alkaloids) were reported by DUŠISNKÝ [6], [7] and MOLNÁR [8].

The samples used for the present experiments were prepared by the solventless Grignard process worked out by PROSZT, NAGY and LIPOVETZ [9], [10]. The apparatus used was the same as described in the previous paper.

For the determination of the rate of hydrolysis of dimethyl diethoxy-silane, the supporting electrolyte was a 0.25 M phosphate buffer of pH 7.0, containing 10% ethyl alcohol. A buffer of relatively high concentration had to be used to insure sufficient conductivity of the supporting electrolyte. The determinations were carried out at $20.00 \pm 0.05^\circ\text{C}$. The concentration of the added dimethyl diethoxysilane was 1.10^{-2} M. The decrease of the concentration brought about by hydrolysis was followed by observing the decrease of the incision on the oscillopolarographic $dE/dt = f(E)$ curves by taking from time to time a photograph of the oscillogram. A set of data thus obtained is illustrated in Fig. 1. Concentration and its logarithm were plotted against time. The logarithmic plot results in a straight line, thus showing the reaction to be of the first order with respect to dimethyl diethoxy-silane under the experimental conditions used. On the basis of the above results a half-time of 44 minutes is obtained. By using the well-known formula for first-order reactions

$$k = \frac{\ln 2}{t^{1/2}}$$

the value of the rate constant is found to be $1.57 \cdot 10^{-2}$ minute $^{-1}$ under the conditions employed.

As preliminary experiments, similar measurements were made with phenyl triethoxysilane. The decrease of the incision with time could also be

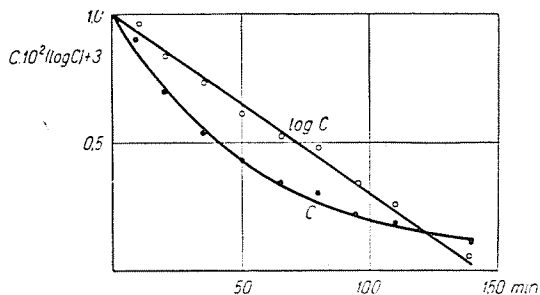


Fig. 1. Concentration of dimethyl diethoxysilane plotted against time

observed in this case (Fig. 2). The figure shows only the cathodic branch of the oscillograms; the successive curves were photographed after one-hour periods of waiting.

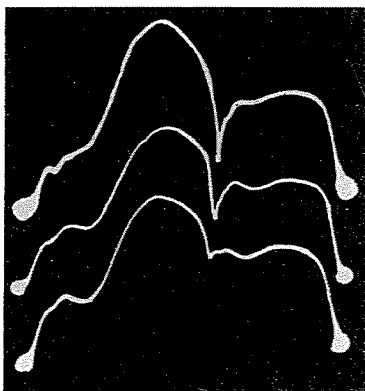


Fig. 2. Oscillograms of phenyl triethoxysilane, recorded after intervals of 1 hour (only the cathodic branches of the curves are reproduced)

In the future a systematic study of the kinetics of hydrolysis of the compounds mentioned in the previous paper [4], [5] will be made.

* * *

The author is indebted to Prof. J. Proszty, and Dr. J. Nagy for their valuable advice, further to Dr. J. Nagy and Mrs. L. Pálóssy for having kindly made the test substances available.

Literature

1. REUTHER, H.: Zeitschr. f. anorg. allgem. Chemie **272**, 122 (1953).
2. SHAFFER, L. H. and FLANIGEN, E. M.: Journ. Phys. Chem. **61**, 1591 (1957).
3. SHAFFER, L. H. and FLANIGEN, E. M.: Journ. Phys. Chem. **61**, 1595 (1957).
4. DAMOKOS, T.: Chemické Zvesti (in press).
5. DAMOKOS, T.: Magyar Kém. Folyóirat **68**, 175 (1962).
6. DUŠINSKÝ, G.: Chemické Zvesti XIV. 764 (1960).
7. DUŠINSKÝ, G.: Ceskoslov. Farm. **10**, 181 (1961).
8. MOLNÁR, L.: Lecture held at the International Conference for Analytical Chemistry, Budapest, 1961.
9. NAGY, J.: Periodica Polytechnica **2**, 241 (1958).
10. PROSZT, J., LIPOVETZ, I. and NAGY, J.: Hungarian Patents PO-126—668; PO-146—825.

T. DAMOKOS; Budapest, XI., Gellért tér 4. Hungary.