acids are not available. Thus, as a result of their shortage of fats and oils during the war, the Germans used a linseed oil soap in the manufacture of Buna. This actually served a real function yet it did greatly slow down their production. Later when even this became unavailable they used synthetic fatty acid prepared by the oxidation of Fischer Tropsch paraffin.

Research work in this country has shown that synthetic rubber can be made from polyunsaturated acids and other low grade fatty acids at present production rates if special activators are used to compensate for the inhibiting effects. However, these types of rubber have never been tested extensively on a commercial scale and do introduce a number of new difficulties into the manufacturing operations.

Trends in the Manufacture of Soaps for Use in Making Synthetic Rubber

There has been a noticeable trend in the fatty acids or soaps used in the manufacture of synthetic rubber. At first distilled myristic and palmitic acid from spermaceti was used. This was replaced soon by distilled myristic acid from coconut fatty acids. When the supply of this became short, soap made from selectively hydrogenated tallows and greases was used. Large scale manufacture of GR-S necessitated larger quantities of soap. This was obtained first from high grade edible tallow and finally from hydrogenated oils, tallows, and greases.

Future developments point to the use of highly purified fatty acids or soaps having a definite ratio of the various fatty acids present. Crystallized acids are quite satisfactory and uniform in their activity. For example, crystalline palmitic acid would be desirable in certain cases while for others a crystallized high purity oleic acid free from polyunsaturates would be ideal. Improvement in crystallization processes and development of markets for the polyunsaturated acids obtained as by-products will help to bring these things to pass. Proper economic analysis of the technological progress in the related fields will certainly determine the course of the future in this field.

The author wishes to acknowledge the assistance obtained from the unpublished summaries and specifications contributed by the scientists and companies who have participated in the synthetic rubber program.

REFERENCES

1. Fryling, C. F., and Harrington, E. W., Ind. Eng. Chem., *36*, 117 (1944).
2. McBain, J. W., and Soldate, A. M., J. Am. Chem. Soc., *64*, 1556 (1942).
3. McBain, J. W., Private communication to Rubber Reserve, March 22, 1943.
4. Harkins, W. D., Heller, W., *et al.*, Private communication to Rubber Reserve, June 24, 1943.
5. Harkins, W. D., J. Chem. Phys., *13*, 381 (1945).
6. Willson, E. A., Private communication.
7. Fryling, C. F., Private communication to Rubber Reserve, 5-21-42.
8. Cuthbertson, G. R., Coe, W. S., and Brady, J. L., Ind. Eng. Chem., *38*, 975 (1946).
9. Hendricks, J. G., India Rubber World, *114*, 60 (1946).
10. Rubber Reserve specification limits for soap.
11. Pfau, E. S., Wilson, J. W., *et al.*, April to Nov., 1943, Private communication to Rubber Reserve, March 13, 1944.
12. Semon, W. L., Private communication, March, 1941.
13. Rubber Age, *59*, 198 (1946); 1945 Report of Bureau of Ag. and Ind. Chem. of USDA.
14. Fryling, C. F., U.S.P. 2,366,325 to the B. F. Goodrich Company, January 2, 1945.

The Hydrolysis of Fatty Acid Chlorides

S. T. BAUER and MAIZIE C. CURET

Southern Regional Research Laboratory[1]
New Orleans, Louisiana

IN the course of the preparation of a series of synthetic glycerides of known molecular configuration it was necessary to store the acid chloride (1) intermediates for various periods of time. The freshly distilled acid chlorides were stored in sealed glass ampoules and analyzed prior to use. After several months of storage under these conditions no appreciable hydrolysis could be detected. It was realized, however, that under commercial conditions of storage more or less hydrolysis might occur from the presence of moisture, and it appeared advisable, therefore, to determine the relative rates of decomposition of the more commonly used saturated and unsaturated fatty acid chlorides.

A search of the literature revealed little information on the relative rates of hydrolysis of acid halides. Velasco and co-workers (4, 6) investigated the velocities of hydrolysis of acetyl chloride, chloroacetyl chloride, propionyl chloride, and butyryl chloride. The degree of hydrolysis was determined by measuring the extent of diffusion of the reaction products into water and toluene at 25° C. and 45° C. These investigators reported that hydrogen ions do not catalyze any of the hydrolytic reactions of the chlorides, which would indicate that the mechanism of hydrolysis in this case is different from that of the esters and amides of the fatty acids. Similar results have been reported by Velasco and Ollero (5) and by Karvé and Dolé (2, 3) with respect to the rates of hydrolysis of a number of aromatic acid chlorides. The acid halides used by the latter investigators were dissolved in chloroform or benzene and shaken with water at a constant rate. Hydrolysis was found to occur at the boundary between the two liquid phases at rates which were determined by diffusion of the reactants and reaction products across the interfacial boundary. The rate constants were found to increase with increasing concentration of acid halide. The hydrochloric acid formed during hydrolysis was found to exert no catalytic action. Conical flasks were said to favor the hydrolysis.

Since there are no available data on the hydrolysis of the higher fatty acid chlorides, experiments were made to determine the hydrolysis of a number of saturated and unsaturated fatty acid chlorides when shaken with water for varying periods of time.

Experimental

Purification of the Fatty Acids and Preparation of Fatty Acid Chlorides. The saturated and unsaturated fatty acids, with the exception of octanoic and decanoic, were purified by the method described by Bauer (1). Commercial preparations of octanoic and

---

[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

TABLE 1

Hydrolysis of Saturated Fatty Acid Chlorides

Time Minutes	Fatty acid chlorides					
	Octanoyl	Decanoyl	Lauryl	Myristyl	Palmityl	Stearyl
	Mole % unhydrolyzed	Mole % unhydrolyzed	Mole % unhydrolyzed	Mole % unhydrolyzed	Mole % unhydrolyzed	Mole % unhydrolyzed
5	93.0	96.7	96.3	98.4	95.6	89.0
15	79.8	92.4	95.2	95.4	89.9	14.0
30	63.4	86.2	94.0	90.8	82.8	7.7
60	48.0	73.8	90.1	84.1	57.2	2.2
120	34.6	58.9	79.0	74.0	25.3	1.8
180	35.1	50.7	72.2	55.5	3.3	0.1
240	32.8	45.6	65.8	45.8	1.7	1.2
300	32.2	45.2	55.7	37.3	3.0	0.9
360	32.7	44.5	51.4	32.5	2.7	1.8
420	30.7	44.7	43.4	25.2	2.5	1.6
480	27.7	42.7	40.4	19.0	3.8	......
720	......	......	27.4	4.4	......	......
960	......	......	27.1	4.2	......	......
1440	......	......	16.9	3.4	......	......
1920	......	......	13.09	3.4	......	......
2160	......	......	13.99	......	......	......
2880	......	......	14.20	......	......	......

decanoic acids were fractionally distilled, and that fraction selected whose neutralization equivalent corresponded most nearly to the theoretical value.

The acid chlorides were prepared by reaction of the fatty acids with a suitable chlorinating agent according to previously described methods (1). The acid chloride was distilled and sealed in glass ampoules until used. The purity of each preparation was determined by weighing a one-gram sample of the acid chloride into a 50-ml. glass-stoppered Erlenmeyer flask to which was added 20 ml. of a 20% aniline-ether solution. After the reaction was completed, 2 ml. of concentrated hydrochloric acid was added to convert the excess aniline to the hydrochloride. The ether was removed by evaporation on the steam bath and the aniline hydrochloride and mineral acid were removed by washing the anilide repeatedly with distilled water. The free fatty acid content of the anilide solution was determined by dissolving the product in 25 ml. of hot neutral alcohol and titrating the solution with 0.1 N sodium hydroxide. Analysis of the acid chlorides used in this work indicated a purity of 99.2% or better on the assumption that free fatty acid was the only impurity present.

Hydrolysis of the Fatty Acid Chlorides. A portion (approximately 0.9-1.0 g.) of acid chloride was weighed into a 50-ml. glass-stoppered Erlenmeyer flask which was placed on a mechanical agitator. A glass bead was added to the flask and 5 ml. of distilled water was added from a pipette. The agitator used was a modification of Camp's shaking apparatus which imparted a planetary motion to the contents of the flasks through a pulley-driven shaking platform.

The acid chloride-water mixture was shaken at room temperature (25° C.) for various intervals of time after which the reaction was stopped by the addition of 10 ml. of a 20% aniline-ether solution to convert the unhydrolyzed portion of acid chloride to the corresponding anilide.

The free fatty acid content of the anilide-fatty acid mixture was determined by titration with one-tenth normal sodium hydroxide solution. Since any free fatty acid which may have been present in the original chloride is titrated along with that produced by hydrolysis, the observed value of the latter must be corrected by subtraction of the previously determined value for the former.

TABLE 2

Hydrolysis of Unsaturated Fatty Acid Chlorides

Time Minutes	Fatty acid chloride		
	Elaidyl	Oleyl	Linoleyl
	Mole % unhydrolyzed	Mole % unhydrolyzed	Mole % unhydrolyzed
5	97.6	98.9	97.2
15	94.8	96.9	89.8
30	91.1	95.2	82.4
60	88.0	67.8	73.0
120	78.4	29.7	64.0
180	71.1	21.5	50.5
240	62.5	18.9	46.0
300	50.4	20.7	44.0
360	47.7	21.5	46.6
420	39.2	21.2	45.9
720	12.9	16.3	......
960	1.3	......	......
1440	1.5	......	......
1920	......	11.98	......
2160	......	......	......
2880	0.5	......	......

In order to compare the relative rates of hydrolysis of the acid chlorides it is necessary to express the results on a mole percentage basis. This may be done by means of the following equation:

Mole per cent of unhydrolyzed acid chloride equals

$$\frac{\text{moles original acid chloride} - (\text{moles NaOH} - \text{moles free fatty acid in original acid chloride})}{\text{moles original acid chloride}} \times 100$$

or

$$\frac{\dfrac{W_s - W_a}{\text{M. W. chloride}} - \left(\dfrac{\text{ml. NaOH} \times \text{normality}}{1000} - \dfrac{W_a}{\text{M. W. acid}}\right)}{\dfrac{W_s - W_a}{\text{M. W. chloride}}} \times 100$$

where W_s = weight of sample, and W_a = weight of free fatty acid in the original sample of acid chloride used for hydrolysis.

TABLE 3

Specific Reaction Rate Constants for Hydrolysis of Fatty Acid Chlorides at 25° C.*

Reaction time	Fatty acid chlorides								
	Octanoyl	Decanoyl	Lauryl	Myristyl	Palmityl	Stearyl	Elaidyl	Oleyl	Linoleyl
Minutes	$k \times 10^3$	$k \times 10^3$	$k \times 10^3$	$k \times 10^3$	$k \times 10^3$	$k \times 10^3$	$k \times 10^3$	$k \times 10^3$	$k \times 10^3$
5	14.52	6.71	7.54	3.22	9.00	23.31	4.86	2.21	5.68
15	15.04	5.27	3.28	3.14	7.10	131.1	3.56	2.10	7.17
30	15.19	4.95	2.06	3.22	6.29	85.5	3.11	1.64	6.45
60	12.23	5.06	1.74	2.89	9.31	......	2.13	6.48	5.25
120	8.85	4.41	1.96	2.51	11.45	......	2.03	......	5.64
180	......	3.77	1.81	3.27	......	......	1.90	......	3.80
240	......	......	1.75	3.25	......	......	1.96	......	......
300	......	......	1.95	3.29	......	......	2.28	......	......
360	......	......	1.85	3.12	......	......	2.06	......	......
420	......	......	1.99	3.28	......	......	2.23	......	......
480	......	......	1.89	3.46	......	......	......	......	......
720	......	......	1.80	4.35	......	......	2.84	......	......
960	......	......	1.36	3.30	......	......	4.51	......	......
1440	......	......	1.24	2.33	......	......	......	......	......

* Constants determined only to point of apparent equilibrium.

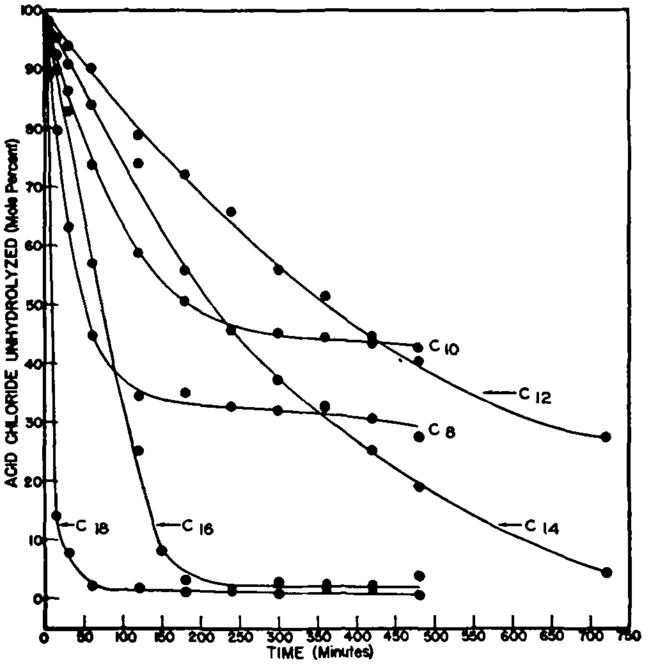

FIG. 1. Hydrolysis of saturated acid chlorides in water at 25° C.

Discussion of Results

Data relative to the hydrolysis of the chlorides of the even-numbered saturated fatty acids from caprylic to stearic are given in Tables 1 and 3 and graphically in Figures 1 and 3. It is evident from the curves in Figure 1 that of the chlorides investigated lauryl chloride is the most resistant and stearyl chloride the least resistant to hydrolysis. Stearyl chloride was essentially completely hydrolyzed after shaking with water for two hours at 25° C., whereas lauryl chloride was hydrolyzed to the extent of only 21% under the same conditions.

Experiments in which weighed amounts of acid chlorides were shaken with 0.1 N hydrochloric acid solution showed that the hydrogen ion had little if any effect on the rate of hydrolysis. Addition of small amounts of free fatty acids to the acid chloride prior to hydrolysis likewise appeared to have no effect on the rate of decomposition of the chloride.

Data with reference to the hydrolysis of the unsaturated fatty acid chlorides are given in Tables 2 and 3 and graphically in Figures 2 and 4. It is apparent from Figure 2 that elaidyl chloride is more resistant to hydrolysis than either oleyl or linoleyl chlorides. The linoleyl and oleyl chlorides hydrolyze at approximately the same rates during the first hour, but thereafter oleyl chloride hydrolyzes more rapidly than linoleyl chloride.

From calculations of specific reaction rates (Table 3) and plots of the logarithms of concentration of acid chloride vs. time, corresponding to various times of reaction (Figures 3 and 4), it appears that acid chlorides undergo hydrolysis in water to a point of apparent equilibrium. This equilibrium appears to take place after about 15 minutes of hydrolysis for stearyl chloride, 30 minutes for octanoyl chloride, 60 minutes for decanoyl and palmityl chlorides, 960 minutes (16 hours) for lauryl chloride, and 1,440 minutes (24 hours) for myristyl chloride. The unsaturated acid chlorides reach the point of equilibrium at 60 minutes for oleyl chloride, 180 minutes for linoleyl chloride, and 960 minutes for elaidyl chloride.

Several hypotheses may be advanced to explain the difference in the rates of hydrolysis between the C_8 to C_{12} and the C_{12} to C_{18} saturated acid chlorides and the apparent equilibrium reached in the case of the shorter chain compounds. The decrease in the reaction rates of the fatty acid chlorides from C_8 to C_{12} may be attributed to decreasing activity of the acid chlorides with increasing chain length. The increasing reaction rates of the fatty acid chlorides from C_{12} to C_{18} is probably due to the increase in melting point and decrease in solubility of the fatty acids, liberated by hydrolysis, in the unhydrolyzed fatty acid chloride. This would result in a more complete withdrawal of the reaction products from the interface at which the reaction occurs. The fact that the hydrolysis of the shorter chain fatty acid chlorides reaches an apparent equilibrium before the acid chloride is completely hydrolyzed indicates the probable formation of a mono-molecular layer of free fatty acid at the interface which inhibits contact between the unhydrolyzed acid chloride and water. Further experimental data would be required to substantiate these hypotheses.

Summary

Fatty acid chlorides of octanoic, decanoic, lauric, myristic, palmitic, stearic, oleic, elaidic, and linoleic acids were hydrolyzed at 25° C. in water and the amounts of unchanged acid chlorides determined after different periods of reaction.

Contrary to expectations, the chlorides of the longer chain fatty acids, palmitic and stearic, reacted at a more rapid rate than the chlorides of the shorter chain fatty acids. Lauryl chloride appears to be more resist-

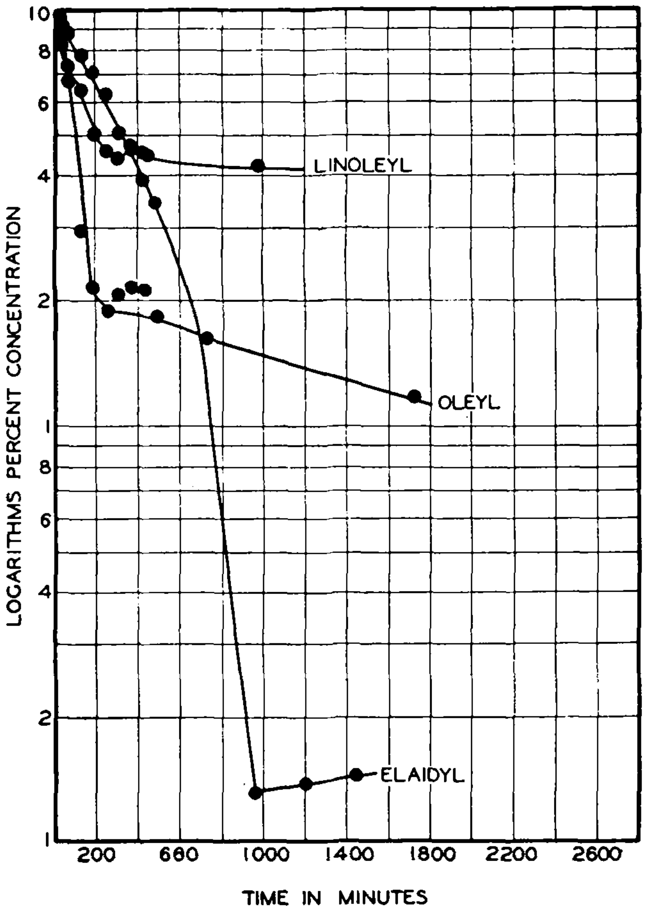

FIG. 2. Hydrolysis of unsaturated acid chlorides in water at 25° C.

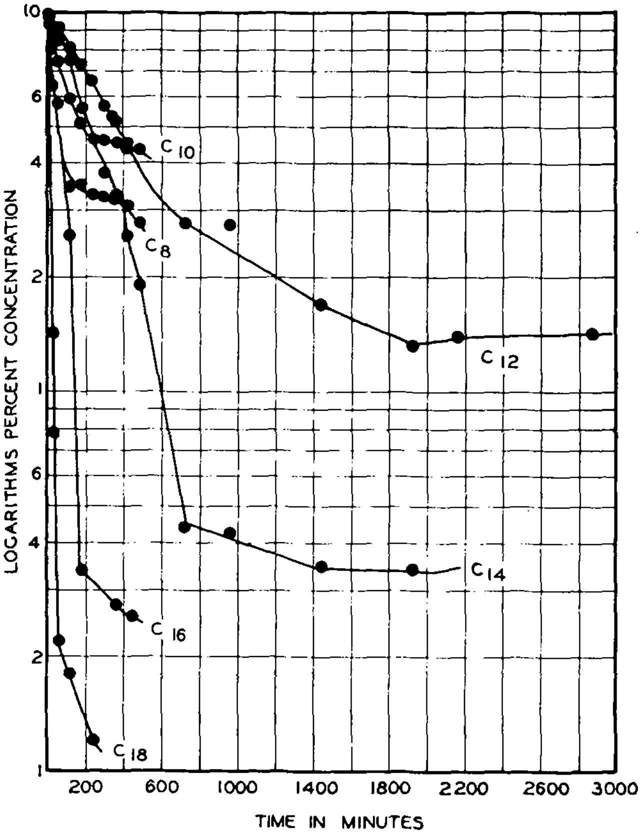

Fig. 3. Hydrolysis of saturated acid chlorides in water at 25° C.

ant to hydrolysis than either the chlorides of the lower molecular weight octanoic and decanoic acids or the chlorides of the higher molecular weight myristic to stearic acids.

The chlorides of the unsaturated acids, oleic, elaidic, and linoleic, are hydrolyzed less rapidly than stearyl chloride. However, elaidyl and myristyl chlorides exhibit the same relative rates of hydrolysis during the first two hours of reaction. Myristyl chloride hydrolyzes more rapidly than elaidyl chloride after the first two hours.

The addition of either hydrochloric acid or free fatty acids to the reaction mixture was found to have no pronounced effect on the hydrolysis of the acid chlorides.

REFERENCES

1. Bauer, S. T., Oil & Soap, *23*, 1-5 (1946).
2. Karvé, Dinakar and Dolé, Krishnaji Khando, J. Indian Chem. Soc., *12*, 733-9 (1935).
3. Karvé, Dinakar and Dolé, Krishnaji Khando, J. Univ. Bombay, *7*, pt. 3, 108-25 (1938).
4. Velasco, J. R., and de la Borbolla, J. R., Anales soc. españ. fís. quím., *34*, 179-97, 603-636 (1936).
5. Velasco, J. R., and Ollero, A., *Ibid.*, *34*, 911-18 (1936).
6. Velasco, J. R., and Ollero, A., *Ibid.*, *35*, 76-83 (1937).

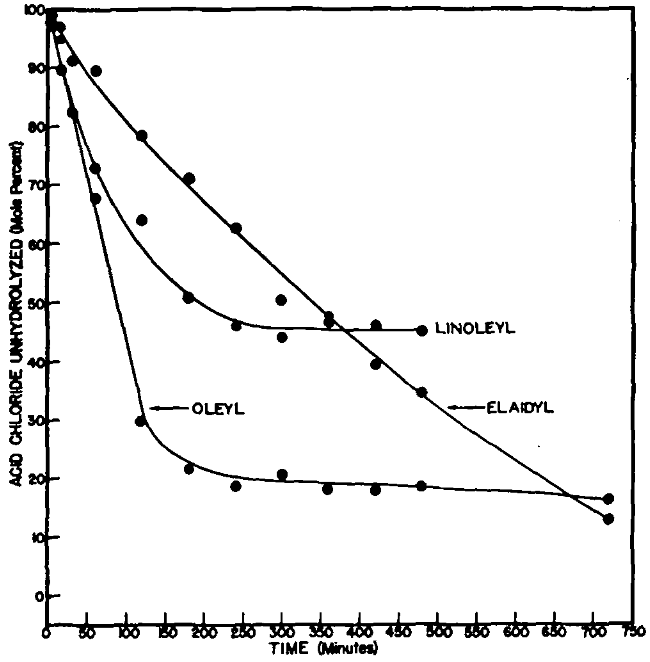

Fig. 4. Hydrolysis of unsaturated acid chlorides in water at 25° C.

A Study of Rancidity of Olive Oils

S. A. KALOYEREAS

Louisiana State University, Baton Rouge, Louisiana

INVESTIGATION of the problem of rancidity is rendered difficult by the fact that the ultimate standards to which all data must be referred are based on taste and smell. Among the aims of these experiments were: a) the comparison of the various known chemical tests for rancidity of fats and oils with the organoleptic test for the purpose of selecting the most reliable one for further use as a standard of reference; b) determination whether olive oils from different localities have different susceptibility to fat oxidation and the study of the effect of various factors and treatments upon such susceptibility to oxidation; and c) determinations whether anise seeds and mustard seeds have antioxidant value for olive oil.

The methods used were the following:

Oxidizability-value developed by Issoglio and modified by Kerr (1), which gives the amount of water-soluble oxidizable substances expressed in O_2/100 gm. of oil.

The Kreis (2) test which is based on the presence in rancid fats of epihydrin aldehyde, an oxidation product of acrolein. It consists in the treatment of the oil with hydrochloric acid and a solution of phloroglucinol in ether.

Fellenberg (3) test based on the presence of aldehydes in the oxidized fats. Vintilescoo and Popesco (4) test based on the presence of peroxides and oxides formed during the development of rancidity.

The Wheeler's (3) iodimetric method of determining the peroxides formed in rancid fats.

The last method was carried out as follows: five g. of olive oil were dissolved in 50 ml. of a mixture of glacial acetic acid and chloroform (3:2 by volume), after which one ml. of saturated potassium iodide solution was added. The mixture was stirred by giving a rotary motion to the flask. Exactly one minute after addition of the potassium iodide, 100 ml. of water were added and the liberated iodine titrated with 0.01 *N* sodium thiosulphate, using starch as