

182. Liquid-phase Reactions at High Pressures. Part I.
Hydrolysis of Esters, and the Knoevenagel Reaction.

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Foreword by WILLIAM A. BONE and JOCELYN F. THORPE.

THE investigations embodied in this paper originated in representations made by us conjointly to the Research Council of Imperial Chemical Industries during 1932—33 to the effect that, having regard to the properties of high-tensile alloy steels available, no difficulty should be encountered in making and installing a complete laboratory apparatus for the explorative study of the effects of pressures up to 20,000 atmospheres upon organic chemical reactions in the liquid phase, according to a scheme submitted.

Eventually, in July, 1933, it was arranged that such an investigation should be undertaken, under grants from Imperial Chemical Industries Ltd., in the High Pressure Research Laboratories at the Imperial College, London, on the understanding that while Professor Thorpe, with Dr. Linstead, would be responsible for the organic chemical aspects of the work, Professor Bone, with Dr. D. M. Newitt, would be responsible for the high-pressure side of it.

Accordingly, an apparatus for pressures up to 5000 atm. was installed for the purpose, and work with it was begun in January, 1934, a further apparatus for pressures up to 20,000 atm. being added about a year later.

IN recent years the effect of pressures of 3000 atm. and more on certain specific chemical reactions in the liquid phase have been investigated by Cohen, Bridgman, Conant, Tamman and others, and a more general survey has been made by Fawcett, Gibson and their collaborators (J., 1934, 386, 396; *Proc. Roy. Soc.*, 1935, A, 150, 223; 1936, 154, 684). Earlier work is summarised in the first of these references.

We commenced by exploring a considerable number of reactions with the object of discovering those which showed large responses to pressures of the order of 5000 atm. No accurate quantitative measurements were attempted. The main positive responses were found in reactions of three classes :

(a) Hydrolysis of esters (and esterification of acids) ; (b) the Knoevenagel condensation and allied reactions ; (c) polymerisation. The present paper deals with the investigation of the first two of these, the principal results being summarised below.

Hydrolysis and Esterification.—The system acetic acid + ethyl alcohol \rightleftharpoons ethyl acetate + water is a classical example of a reversible bimolecular reaction, the equilibrium standing at about 66% esterification and being independent of temperature (Berthelot and St. Gilles, *Ann. Chim. Phys.*, 1862, 65, 385; 66, 1; 68, 225). We found the same position of equilibrium at 5000 atm. pressure and 60°. It is of historical interest that Berthelot and St. Gilles observed no shift in equilibrium at a pressure of about 100 atm. (*loc. cit.*, 66, p. 45). The constancy of this value is not surprising in view of the similarity between the molecular volumes of the two pairs of reactants. The effect of pressures of 500, 2000, 3500, 5000 and 6500 atm. on the velocity of this reaction at 60° in the absence of catalyst is shown in Table I and in Fig. 1. There is a large positive response. At 6500 atm. the system passes more than half way to equilibrium, under conditions which give a very small amount of esterification at atmospheric pressure. In Fig. 1 the percentage of acid esterified is plotted against $\log(1000/t)$ for the various pressures, giving a series of approximately parallel lines. The approximate absolute velocity constants for the forward reaction were calculated, the value 4.0 being used for the equilibrium constant, and corrected for increase in concentration due to compressibility of the mixture. The values of k , in mols./l.-sec., are :

| | | | | | | |
|-----------------------|-------|-------|-------|-------|------|-------|
| Pressure, atm. | 1 | 500 | 2000 | 3500 | 5000 | 6500 |
| $k \times 10^7$ | 3.031 | 4.256 | 11.87 | 29.85 | 76.9 | 168.2 |

We are endeavouring to obtain more precise information on this point.

Hydrolysis at room temperature. At 17° ethyl acetate was not appreciably hydrolysed by water at 5000 atm. pressure, but the hydrolysis by dilute mineral acid showed a positive response.

FIG. 1.

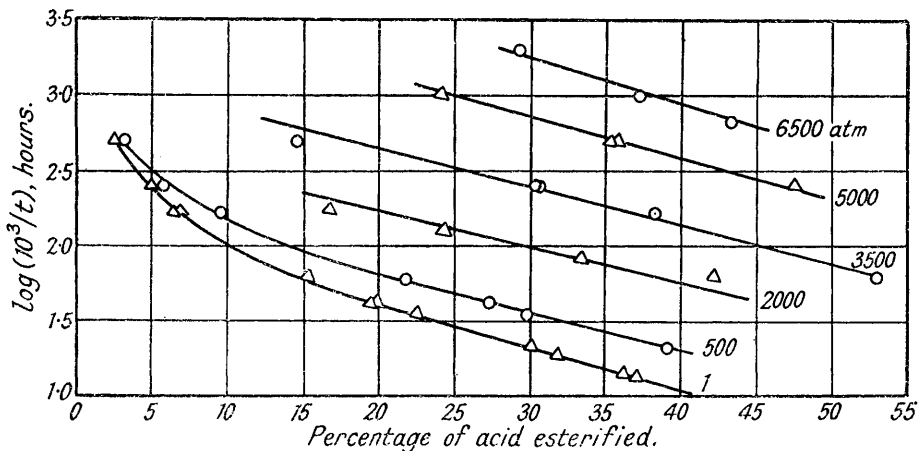


TABLE I.

Esterification of Equimolecular Mixtures of Acetic Acid and Ethyl Alcohol at 60°.

| Time (hours). | Acid esterified, %, at (atmospheres). | | | | | | Time (hours). | Acid esterified, %, at (atmospheres). | | | |
|---------------|---------------------------------------|------|-------|------------|------------|-------|---------------|---------------------------------------|------|-------|-------|
| | 1. | 500. | 2000. | 3500. | 5000. | 6500. | | 1. | 500. | 2000. | 3500. |
| 0.5 | — | — | — | — | — | 29.2 | 16 | — | — | — | — |
| 1.0 | — | — | — | — | 24.0 | 37.2 | 17 | — | 21.7 | — | — |
| 1.5 | — | — | — | — | — | 43.2 | 24 | 19.8 | 27.2 | — | — |
| 2 | 2.7 | 3.3 | — | 14.4 | 35.3, 35.8 | — | 28 | 22.3 | — | — | — |
| 3 | — | — | — | — | 46.5 | — | 29 | — | 29.8 | — | — |
| 4 | 4.8 | 5.7 | — | 30.2, 32.6 | 47.3 | — | 48 | 30.1 | 39.1 | — | — |
| 6 | 6.9 | 9.4 | 16.7 | 38.6 | — | — | 53 | 31.8 | — | — | — |
| 8 | — | — | 24.2 | — | — | — | 71 | 36.0 | — | — | — |
| 12 | — | — | 33.3 | — | — | — | 77 | 37.0 | — | — | — |

The ease of hydrolysis of many ethyl esters by water alone, or by dilute acids, was very strikingly increased by the application of pressure. For instance, ethyl oxalate, cyanoacetate, and chloroacetate, when in the pure state, were not appreciably hydrolysed by water at room temperature and atmospheric pressure during 3–4 days, although a very slow reaction could be detected later, catalysed by the acid formed. Under a pressure of 5000 atm. and at 17° ethyl oxalate was hydrolysed to the extent of 50% in a day, and the reaction was nearly complete in a week (see Table II). Apart from certain polymerisations observed by Conant and by Fawcett and Gibson, this seems to be the most striking positive effect so far achieved in liquid-phase reactions at high pressure. The pressure hydrolysis was doubtless facilitated by the separation of solid oxalic acid dihydrate which was observed during the later stages. The hydrolyses of ethyl chloroacetate, cyanoacetate, and trichloroacetate by water alone showed considerable although less marked responses to high pressure. Cyanoacetic acid cannot readily be isolated by the hydrolysis of its ester by the usual methods, but this can easily be achieved by hydrolysis with water alone or with dilute acid under a pressure of 5000 atm. The esterification of chloroacetic acid is also facilitated at high pressure.

Ethyl malonate was not hydrolysed at room temperature by water alone at 5000 atm. pressure, but hydrolysis by dilute solutions of hydrochloric or malonic acid was accelerated. The hydrolysis with mineral acid yielded a mixture of half ester and acid. Ethyl diethylmalonate behaved similarly. The hydrolysis by dilute acid of two typical natural mixtures of mixed glycerides represented by linseed oil and soya-bean oil showed a positive response

TABLE II.

Hydrolysis of Ethyl Esters at Room Temperature.

(3 Mols. of water per mol. of ester group were added in every case.)

| Ester (1 mol.). | Mols. per ester group of | | Experimental conditions. | | | Hydrolysis, %. | |
|------------------|---------------------------------------|---------|-------------------------------|-------|-----------------|---------------------|--------------|
| | EtOH. [Sufficient for solution] | HCl. | Press., <i>P</i> , in atm. | Temp. | Time, hours. | At <i>P</i> atm. | At 1 atm. |
| Oxalate | — | — | 5000 | 16° | 3 | 5 | 0·0 |
| | | | 5000 | 16 | 24 | 50 | 0·0 |
| | | | 5000 | 17 | 96 | 80 | 1·7 |
| | | | 5000 | 17 | 168 | 90 | 4·8 |
| Acetate | 0·75 | — | 5000 | 17 | 240 | 0·6 | 0·0 |
| | 0·75 | 0·025 | 5000 | 17 | 24 | 41·4 | 18·7 |
| | 0·75 | 0·025 | 5000 | 23 | 72 | 43·1 | 39·5 |
| Malonate | 1·5 | — | 5000 | 18 | 72 | 0·0 | 0·0 |
| | 1·5 | 0·025 | 5000 | 22 | 72 | 37·5 | 11·1 |
| Succinate | 1·5 | — | 5000 | 17 | 72 | 0·0 | 0·0 |
| Ethylmalonate | 1·5 | 0·025 | 5000 | 24 | 72 | 14·8 | 1·0 |
| Cyanoacetate | 1·5 | — | 5000 | 17 | 96 | 3·4 | 0·5 |
| | 1·5 | — | 5000 | 18 | 240 | 16·7 | 1·4 |
| Chloroacetate | 1·5 | { 0·005 | 5000 | 21 | 24 | 5·9 | 1·2 |
| | | { 0·025 | 5000 | 21 | 24 | 22·0 | 3·2 |
| | 2·0 | — | 1000 | 21 | 72 | 0·5 | 0·3 |
| | 2·0 | — | 2050 | 21 | 72 | 1·8 | 0·3 |
| | 2·0 | — | 2900 | 19 | 72 | 3·7 | 0·3 |
| | 2·0 | — | 4000 | 18 | 72 | 7·2 | 0·3 |
| Trichloroacetate | 2·0 | — | 5000 | 18 | 72 | 14·8 | 0·3 |
| | 2·75 | — | 5000 | 23 | 72 | 48·9 | 15·3 |

to high pressure. The accelerated hydrolysis of fats by alkali under pressures of the order of 100 atm. is already known and forms the subject matter of patented processes. On the other hand, tristearin could not be hydrolysed by water, dilute acid, or dilute alkali at 5000 atm. and at room temperature; neither could positive indications be obtained of the hydrolysis of ethyl benzoate and ethyl succinate. The results are summarised in Table II.

Knoevenagel and Allied Reactions.—The reaction between cyanoacetic ester and various cyclic ketones was selected for study because some information was already available on the speed of the reaction at atmospheric pressure, and because the velocity could conveniently be altered by varying the amount of the catalyst, piperidine (Barrett and Linstead, J., 1935, 436).

High pressures were found to have a very considerable effect on these condensations. In the presence of 0·05 mol. of piperidine, *cyclopentanone* and cyanoacetic ester at atmospheric pressure and 18° yielded 3% of *cyclopentylidenecyanoacetic ester* in 30 minutes. Under the same conditions of temperature and concentration but at 5000 atm. pressure the yield was 50%, and at 15,000 atm. the condensation was practically complete. The reaction was inconvenient, however, in that the reaction mixture solidified, and the containing tubes tended to fracture on release of the pressure. The analogous condensation with *cyclohexanone* was free from this defect, and showed a similar response to the application of pressure (Table III). No condensation could be observed between *cyclohexanone* and

TABLE III.

cycloHexanone + Cyanoacetic Ester with and without Piperidine.

| Piperidine, mols. | Temp. | Press. (atm.). | Time (hours). | Yield of ethyl <i>cyclohexylidenecyanoacetate</i> , % of theory. | |
|----------------------|-------|-------------------|------------------|---|--------------------------|
| | | | | Under pressure. | At atmospheric pressure. |
| 0·05 | 18° | 4000 | 0·5 | 72 | 38·5 |
| 0·025 | 18 | 4000 | 0·5 | 65·5 | 20·6 |
| — | 18 | 4000 | 0·5 | Nil | Nil |
| — | 60 | 3200 | 50 | 11·7 | „ |
| — | 60 | 3200 | 124 | 13·2 | „ |
| — | 60 | 5000 | 80 | 26·3 | „ |

cyanoacetic ester at atmospheric pressure in the absence of a catalyst. It was therefore of great interest to find that these reagents yielded *cyclohexylidenecyanoacetic ester* at 60°

and 5000 atm. pressure without the addition of piperidine. In view of the fact that *cyclohexanone* failed to condense with either malonic or acetic ester under these conditions, it is possible that the nitrogenous group of either the original cyano-ester or the condensation product, acting in the imino-phase as a base, catalyses the high-pressure condensation.

It has been found that the Knoevenagel condensation is inhibited by substituents adjacent to the ketonic group (Barrett, Cook, and Linstead, J., 1935, 1065). Ethyl 2-methyl-*cyclohexanone*-2-carboxylate fails to react with cyanoacetic ester in the presence of piperidine at atmospheric pressure over long periods. We find that a small but definite degree of condensation occurs in the course of a few days at a pressure of 4000 atm. Dr. A. F. Millidge found the product to be ethyl 2-methyl-*cyclohexylidene*-1-cyanoacetate-2-carboxylate (J., 1936, 484). Ethyl 2-methyl-*cyclohexanone*-2- β -propionate, however, failed to react appreciably with cyanoacetic ester in the presence of piperidine even under a pressure of 5000 atm.

Although *cyclohexanone* failed to condense with ethyl acetate in the presence of piperidine at high pressure, the reaction mixture afforded a poor yield of 2- Δ^1 -*cyclohexanyl-cyclohexanone* (Wallach, *Ber.*, 1907, 40, 70; Kon and Nutland, J., 1926, 3101), formed by condensation of two molecules of the ketone. The same condensation occurred in the absence of diluent, and also, to a slight extent, in the absence of catalyst. *cyclopentanone* condensed with itself in a similar manner at high pressure, but more readily (see Table IV). The product was 2-*cyclopentylidene*-*cyclopentanone*, identical with that prepared by Wallach's method (*Ber.*, 1896, 29, 2963). Self-condensation of ketones of this type in the presence of piperidine has not previously been observed, and we could detect no condensation in control experiments at atmospheric pressure.

TABLE IV.

Autocondensation of cycloHexanone and of cycloPentanone under Pressure at 60°.

| Ketone. | Press., atm. | Time (hours). | Diluent (1 mol.). | Quantity of piperidine (mols.). | Yield of unsaturated ketone, % of theory. |
|----------------------------------|-----------------|------------------|----------------------|------------------------------------|--|
| C ₆ H ₁₀ O | 4500 | 120 | EtOAc | — | 1.4 |
| " | 4500 | 120 | Ethyl malonate | — | 2.0 |
| " | 4500 | 120 | EtOAc | 0.05 | 9.0 |
| C ₅ H ₈ O | 4500 | 120 | " | 0.05 | 40.0 |
| C ₆ H ₁₀ O | 4000 | 24 | — | 0.05 | 5 |
| C ₅ H ₈ O | 4000 | 24 | — | 0.05 | 45.5 |
| " | 4000 | 22 | EtOAc | 0.1 | (a) 45, (b) 45 |

Control experiments corresponding with all the above, under identical conditions but at atmospheric pressure, yielded no detectable amount of condensation product in any case.

Fawcett and Gibson's early results were generalised as follows: (1) That reactions which proceeded slowly at atmospheric pressure showed increased velocity at the same temperature under high pressure; and (2) that reactions which did not proceed at atmospheric pressure (in the absence of catalysts) did not proceed at pressures up to 3000 atm. Later work (*loc. cit.*, 1935—36), concerned with a more accurate study of certain reactions, did not affect these main conclusions.

Our results agree with (1), but we have found four reactions, mentioned above, which proceed at pressures of the order of 5000 atm. but are not detectable at atmospheric pressure under the same conditions. Fawcett and Gibson themselves observed an exception to (2) in the condensation and polymerisation of acetaldehyde (*loc. cit.*, 1934). It is obviously difficult in practice to decide whether a given reaction proceeds at atmospheric pressure with a very slow velocity or not at all. The hydrolyses of ethyl cyanoacetate and chloroacetate by water are examples of reactions, accelerated by high pressures, which are just detectable at ordinary temperature and pressure. In any case it is clear that, as a practical generalisation, it is no longer correct to say that liquid-phase reactions which do not proceed at atmospheric pressure also do not proceed at high pressures under otherwise like conditions.

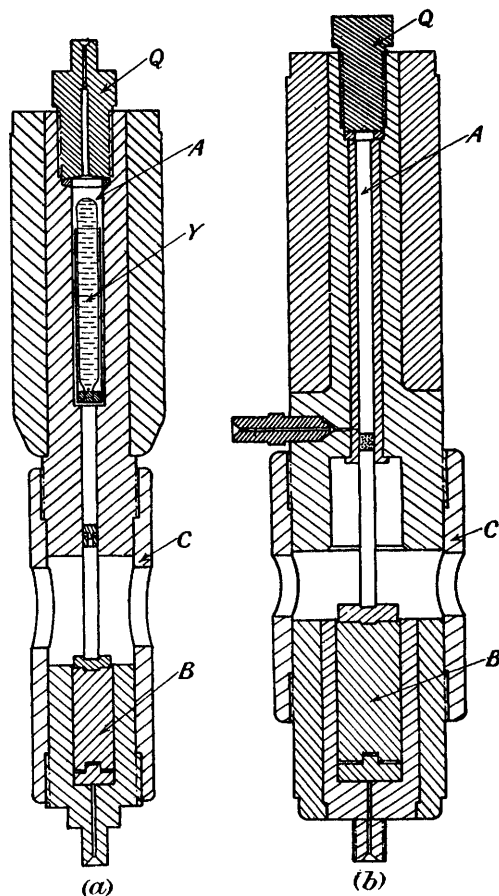
EXPERIMENTAL.

With the aid of modern high-tensile steels the production and maintenance of high pressures is no longer a matter of great difficulty; and provided suitable methods of construction are

adopted, reaction vessels of moderate size may be designed with a suitable factor of safety for pressures of 10,000 atm. and even higher (Newitt, *Trans. Inst. Chem. Eng.*, 1936).

In the work now described two such vessels have been employed capable of withstanding internal pressures of 5000 and 20,000 atm. severally. Both are cylindrical in shape and are built [see Figs. 2 (a) and 2 (b)] by shrinking together two or more steel tubes in such a way that the inner layers of the walls of the resulting compound cylinder are in compression and the outer layers in tension. The curves in Fig. 3 show the calculated distribution of hoop stresses in the walls of the 20,000-atm. vessel before and during the application of the working pressure. It should be noted that at maximum pressure the tensile hoop stresses nowhere exceed 40 tons per sq. inch, a figure providing a satisfactory margin of safety.

FIG. 2.



Each vessel consists of a reaction chamber *A* (Fig. 2) and an intensifier *B* connected by means of a steel sleeve *C*. The reactants are contained in a glass vessel *Y* [Fig. 2 (a)] inverted over mercury in a stainless-steel cup. The remaining free space in the reaction chamber is filled with liquid paraffin, which serves to transmit the pressure to the reactants as the pistons of the intensifier advance.

The method of carrying out an experiment is briefly as follows. The reactants are placed in the upper cylinder *A* (Fig. 4) of the intensifier, which is then filled with liquid paraffin and closed by the end-plug *Q*. By means of the hand pump *N*, a pressure of 1000 atm. is applied through the plug *Q*; the valve *V* is then closed, and pressure is slowly applied to the low-pressure side of the intensifier until the requisite experimental pressure, as measured by the free-piston pressure balance *B* and the gauge *G*, is obtained. Usually this part of the experiment occupies from 5 to 10 minutes, sufficient time being allowed to ensure that the compression is practically isothermal. When the reaction is to be carried out at a temperature above atmospheric, the

chamber is raised to the desired temperature, before introduction of the reactants, by means of an electric furnace, and the temperature is thus maintained throughout the experiment. The

FIG. 3.

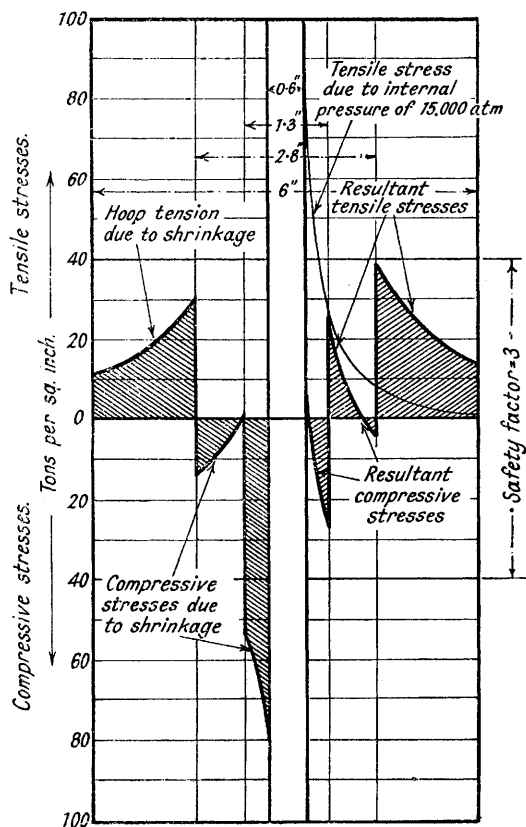
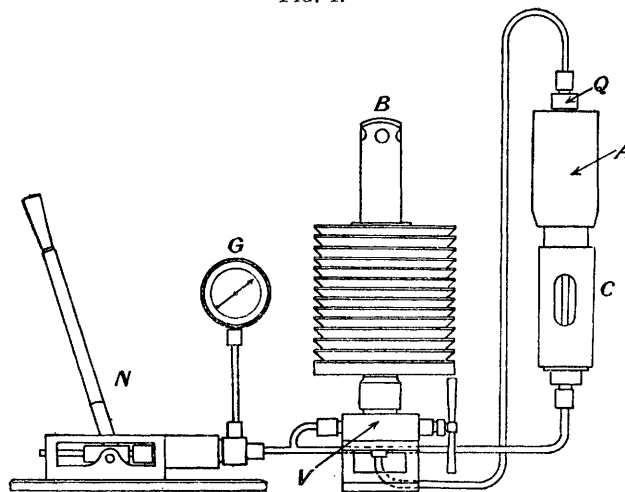


FIG. 4.



pressures indicated by B and G correspond with the ratios of the areas of the pistons of the intensifier, due allowance being made for frictional losses; it is therefore not essential always to employ the pressure balance provided the gauge G is calibrated at frequent intervals. In work-

ing at 15,000 atm., the intensifier was calibrated by the pressure balance up to 5000 atm. and by a manganin resistance gauge to the higher pressure.

Ethyl Acetate-Acetic Acid System.—A.R. Reagents were used. Aliquot portions of the pressure-treated sample were titrated with standard alcoholic potash. A known excess of the potash was then added, the samples were heated under reflux on a steam-bath for 15 minutes (soda-lime guard-tube), cooled, and the excess of alkali estimated with standard acid. In this way the acid and ester present were estimated. Trial experiments showed the method to be satisfactory. When mineral acid was used as catalyst in hydrolyses, an allowance was made in the first titration. The results are summarised in Table I, and the effect of high pressure upon the velocity is shown graphically in Fig. 1.

Experiments on the hydrolysis of ethyl acetate with an excess of water and with dilute acid are summarised in Table II. These show an approach to an equilibrium.

Hydrolysis of Ethyl Oxalate.—The ester was purified by standing over anhydrous potassium carbonate, and was distilled at 76°/11 mm. Analysis by the methods described below showed it to be free from acid. It was not possible to estimate the free acid in a hydrolysed portion by direct titration owing to the rapid hydrolysis of unchanged ester, and the following method was used. The liquid to be analysed was diluted with aqueous alcohol until 25 c.c. contained the equivalent of about 1 g. of ethyl oxalate. The total amount of ester + acid was then estimated by refluxing a 25-c.c. sample for an hour with a known excess of *N*/2-alcoholic potash and back-titrating with standard acid. A second 25-c.c. portion was shaken for 10 minutes with an excess of pure precipitated barium carbonate to neutralise the free acid. The remaining ester was estimated by hydrolysis as before. Separate experiments showed that the presence of the barium salts was not deleterious, and test analyses gave satisfactory results.

A mixture of 1 mol. of ethyl oxalate with 6 mols. of distilled water, and the minimum amount of absolute alcohol (freed from acidic impurities by distillation from quick-lime) needed for miscibility, was left at 17° in the dark. Portions removed at intervals were analysed :

| | | | | |
|--------------------|-----|-----|-----|------|
| Time (days)..... | 4 | 7 | 10 | 21 |
| Hydrolysis, %..... | 1.7 | 4.8 | 9.2 | 33.0 |

No solid separated in these experiments. Similar experiments at 5000 atm. for 3 hours, 1, 4, and 7 days, under otherwise identical conditions, gave the results shown in Table II. A considerable amount of oxalic acid dihydrate (m. p. and mixed m. p. 102°) was formed in the two longest experiments.

Other Ester Hydrolyses.—These are summarised in Table II; the general procedure and analytical methods were those described above for ethyl acetate unless otherwise stated. A few supplementary notes are appended.

Ethyl malonate, free from nitrogenous material, was prepared by the esterification of malonic acid and had b. p. 96°/22 mm. The hydrolysis product obtained from this by the use of dilute hydrochloric acid for 3 days at 5000 atm. and 22° was separated semi-quantitatively by means of sodium bicarbonate into acid and neutral fractions. The proportions of acid and half-ester in the acid fraction were estimated approximately by titration with alcoholic potash. Expressed in terms of ester groups hydrolysed, the hydrolysis was 37.5%. The composition of the product was approximately: malonic acid, 19; ethyl malonate, 43; half-ester, 38%.

Ethyl cyanoacetate, purified by distillation, had b. p. 121°/46 mm., n_D^{20} 1.4170, d_4^{20} 1.0654. Hydrolysis with 3 mols. of water and 1.5 mols. of alcohol for 10 days at 18° and 5000 atm. proceeded to 16.7%. The product was separated into ester and acid by means of sodium bicarbonate. The ester was unchanged in physical properties, and there was no change of the cyano-group. The acid was pure cyanoacetic acid, m. p. and mixed m. p. 68°. The yield of this was 16%, corresponding with the figure obtained by titration. The product from the hydrolysis with *N*/2-hydrochloric acid at 5000 atm. (22% hydrolysis by titration) was separated similarly into pure cyanoacetic ester and acid (20% yield; m. p. 69°; equiv., 85.0; calc., 85.0).

Ethyl chloroacetate (Conrad, *Annalen*, 1877, **188**, 218) had b. p. 142°, n_D^{20} 1.4205, d_4^{20} 1.1498. For analyses of mixtures of acid and ester, the hydrolysis was carried out with *N*/10-aqueous baryta instead of alcoholic potash, to prevent removal of chlorine. Ten minutes' heating on the steam-bath was sufficient for hydrolysis. The product from the hydrolysis with water alone was separated into pure chloroacetic acid, m. p. and mixed m. p. 63°, equiv. 95.0 (calc., 94.5), and ester, b. p. 143°, n_D^{20} 1.4202, d_4^{20} 1.1486. No chloride ion could be detected.

A solution of 1 mol. of chloroacetic acid in 3 mols. of absolute alcohol was submitted to a pressure of 5000 atm. for 3 days at 19°. The ester was formed in 72.7% yield, and had pro-

perties almost identical with those given above. In a control experiment at atmospheric pressure, 26.4% of esterification occurred.

Ethyl trichloroacetate (Spiegel and Spiegel, *Ber.*, 1907, **40**, 1734) had b. p. 74°/28 mm. The mixtures of acid and ester could not be analysed by the methods given above, but the acid could be estimated by direct titration of a known weight of mixture with *N*/10-sodium carbonate (methyl-orange). The product of the pressure hydrolysis (48.9% acid) contained no chloride ion. Trichloroacetic acid (49%) was isolated by separation with sodium bicarbonate.

Ethyl benzoate was completely unaltered by water (10 days) and by dilute hydrochloric acid (7 days) at 18° and 5000 atm. pressure under the same general conditions.

Stearin, prepared from stearic acid by Joglekar and Watson's method (*J. Soc. Chem. Ind.*, 1928, **47**, 365), was made into a thick paste with 30 mols. of water and a small quantity of acetone as a wetting agent. There was no hydrolysis after 6 days at 5000 atm. pressure and 17°. Negative results were also obtained in similar experiments with *N*/10- and *N*/2-hydrochloric acid, and with dilute potash.

Linseed oil (5.9 g., alkali-refined) was dissolved in a mixture of 1.1 c.c. of 0.536*N*-hydrochloric acid, 5 c.c. of ether, and 21 c.c. of acetone. After 6 days at 16° and 5000 atm., there was 9.5% hydrolysis. A control experiment under atmospheric pressure showed 3.7% hydrolysis.

Analogous experiments with water in place of hydrochloric acid gave no hydrolysis either at 1 or at 5000 atm. pressure. Hydrolysis with dilute alkali appeared too rapid for convenient manipulation. Soya-bean oil, treated in exactly the same way as linseed oil, showed 11.2% hydrolysis at 5000 atm. and 2.2% at atmospheric pressure.

Knoevenagel and Other Condensations (see Tables III and IV).—The products were separated by fractional distillation under reduced pressure, and were identified as follows:

*cyclo*Pentylidenecyanoacetic ester: b. p. 180—182°/25 mm., m. p. 57—58° (crude), 58° after crystallisation from alcohol, mixed m. p. 58°.

*cyclo*Hexylidenecyanoacetic ester, from pressure experiments without piperidine: b. p. 150—160°/20 mm., m. p. — 2°, n_D^{20} 1.4960 (crude). Material made with piperidine at atmospheric pressure had b. p. 155—160°/20 mm., m. p. — 1°, n_D^{20} 1.4940, mixed m. p. — 2°.

2- Δ^1 -*cyclo*Hexenyl*cyclo*hexanone, from pressure experiments without piperidine. The crude product, b. p. 143—145°/15 mm., was converted into semicarbazone, and the yield (Table IV) was calculated from the weight of this after drying. After washing with benzene and light petroleum, the semicarbazone melted at 192° alone or admixed with an authentic specimen, m. p. 192°. Kon and Nutland (*loc. cit.*) found that this ketone, b. p. 150°/18 mm., gave a semicarbazone, m. p. 194°, which could be separated by fractional crystallisation into two forms, m. p. 200° and 172°.

2-*cyclo*Pentylidenecyclopentanone, from pressure experiments with piperidine: b. p. 130—140°/15 mm., n_D^{18} 1.5130; semicarbazone, m. p. 210—212° alone, 214—216° in admixture with an authentic specimen, m. p. 222°. Kon and Nutland found b. p. 135°/25 mm., n_D^{19} 1.5215, for the ketone. The yields of this ketone in Table IV are calculated from the weights of dry semicarbazone.

In conclusion we wish to thank Professors Bone and Thorpe, and Imperial Chemical Industries Limited for grants to defray the cost of the apparatus and for maintenance grants.

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