sults are shown in Table II. When only methanol was used as solvent during the interesterification, the results were inconsistent. Addition of another solvent to increase solubility of the fat improved the results. The reaction proceeded rather slowly with most of the fats. However when tricaproin was treated, the characteristic odor of methyl caproate was immediately apparent. The water content of the resin did not markedly affect the course of the reaction since catalyst which had been repeatedly soaked in methanol gave essentially the same results. The amount of monoglyceride found in these experiments was very low. Resin saturated with fatty acid has no catalytic activity. The resin does not catalyze the esterification of free fatty acids with methanol, and saponification of esters occurs to only a negligible extent.

From these observations it appears certain that the free fatty acids have no role in the course of the interesterification.

The interesterification by resin catalysis suggests a strong parallel to the interesterification catalyzed by alkali (8, 9). The heterogeneous system of solid caustic resin and the fat solution may account for the low reaction velocity. The amount of resin used, when expressed in equivalents of alkali, is about four times the amount recommended for interesterification by means of sodium ethylate or sodium hydroxide. A remarkable distinction between the resin catalysis and alkali catalysis is the indifference of the resin catalysis to amounts of water which would interfere with the latter type of reaction.

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# A New Alkali Isomerization Procedure

F. A. VANDENHEUVEL and G. H. RICHARDSON, Fisheries Research Board of Canada, Halifax, Nova Scotia

THE standard procedure described in the 1948 Report of the Spectroscopy Committee (2) has many generally recognized shortcomings. Improvements have been proposed. We are indebted to Brice *et al.* (1) for more adequate spectroscopic constants and for a pertinent suggestion as to the optimum time of reaction. The application of the procedure remained however what it was originally; a long, complicated, exacting series of manipulations requiring above-average skill and experience. Even under the best circumstances the accuracy is in no way remarkable. As a tool in the kinetic study of the alkali-isomerization reactions it is poor. A time lag results from the fact that the sample does not dissolve instantaneously on coming in contact with the hot reagent. This lag cannot be determined because of undefined variations, resulting from the manual handling of the reaction tubes at the time solution takes place. Clearly there was a need for:

a) An apparatus allowing simultaneous application of an identical treatment to samples and blanks
b) A procedure which would eliminate the time lag resulting from delayed solution
c) A procedure allowing the same treatment to be easily reproduced from run to run.

Moreover, to make it a more practical, reliable, and accurate method, steps should be eliminated entirely or extensively modified. Among the steps to be eliminated were:

a) The cumbersome and time-consuming transfer of the reaction mixture to the volumetric flasks
b) The use of specially purified absolute alcohol as solvent.

Among the features needing improvements were:

a) The nitrogen purifying train
b) The handling of the reagent.

The authors undertook the present work in order to find a solution to these problems. The present article describes the outcome as follows:

Under Apparatus:

a) A reagent handling unit allowing preparation, storage, and dispensing
b) A new nitrogen purifying train
c) A new alkali-isomerization apparatus.

Under Determination of $\Delta$ m:

A procedure for the determination of a correction, $\Delta$ m, bearing on the reaction time and allowing lag effects to be eliminated.

Under Suggestion for a New Procedure:

A simple protocol, allowing the faithful reproduction of conditions.

## Apparatus

Figure 1 shows the relative position of each piece of apparatus on the laboratory table (top view). The

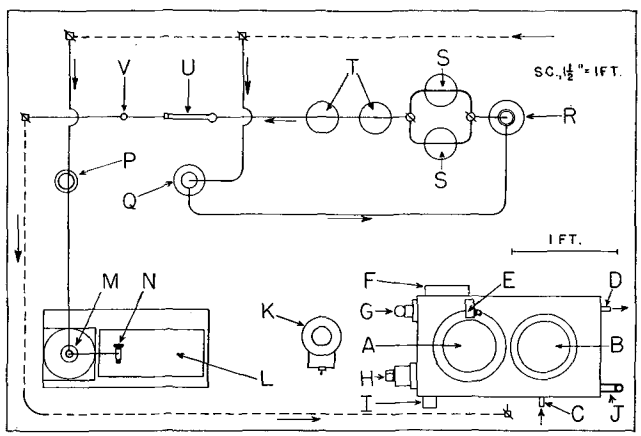


FIG. 1. General lay-out of isomerization equipment.

top half represents the nitrogen purifying train; in the lower half the isomerization apparatus proper is shown at the right while the reagent dispensing unit is shown at the left.

A few details of the isomerization apparatus are indicated: heating bath A, cooling bath B with cooling water inlet C and outlet D, thermoregulator E, duplex female outlet F, pilot light G, selector switch H, relay I, and support J. K is a standard Variac transformer.

Reagent dispensing unit L is composed of the dispenser proper M, installed on a shelf at the proper height to be used in connection with scales L (torsion balance) on which the reagent is weighed out. The dispenser is connected to the nitrogen line through a mercury safety valve P.

The purifying train, following the direction of the stream indicated by arrows, is composed of wet nitrogen scrubber Q, safety bottle or trap R, 10% sulfuric acid absorbers S installed in by-pass, concentrated sulfuric acid absorbers T, soda-lime tube U, flow meter V (Greiner No. C10947 A Florator), and a utilization line ending at the position shown.

The solid lines represent glass connection, the dashed ones small bore brass pressure tubing. The valves indicated by squares are small brass needle valves. The nitrogen supply comes through a standard pressure regulator from a bottle not shown.

The nitrogen scrubber is shown in Figure 2. Reservoir A contains a solution made of equal parts of concentrated aqueous ammonia and saturated aqueous ammonium chloride solution to the level indicated.

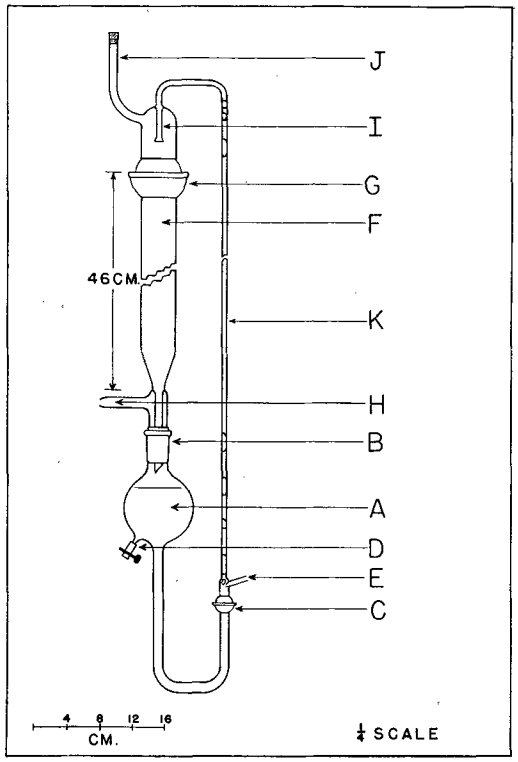


FIG. 2. Nitrogen scrubber.

Joints B (℉ 24/40), C (℉ 18/9), and G (℉ 65/40) allow convenient assembling and cleaning; the latter two are maintained in position by appropriate clamps (not shown). An outlet D is provided for emptying the spent solution. The gas inlet E leads the nitrogen to the 6-mm. section gas-lift K while the nitrogen, after passing through the copper shavings filling F, leaves the scrubber through H for the absorption train.

The copper shavings (Chore Girl) are kept wet by the intermittent spray of solution issuing from I. A filling tube J allows the replacement of the spent solution.

The oxygen-free nitrogen is stripped of water and ammonia in the rest of the train. Most of the ammonia, if not all, is retained in the 10% sulfuric acid absorbers. The solution in these, when saturated, tends to clog the inlet tube, hence the by-pass.

The reagent dispenser is shown in Figure 3. It consists of a reservoir A (2-litre borosilicate glass bottle with 24/40 ℉ neck B), and a tube C which functions either as bubbler (preparation) or siphon (dispenser). A side tube D allows nitrogen pressure to be exerted to lift reagent in C for delivery, through the flow regulating stopcock E, to tip F. As seen from the figure, the tip is protected by a glass spring-fastened, ℉ cap during storage. Bottle A can be heated by a 250-watts resistor H. The latter is maintained in position by two circular collars G, tightly fastened to the bottle. Asbestos-insulated leads I allow connection to a Variac transformer. Bottle A rests on a glass wool pad K. The same material is used to stuff the top space as shown.

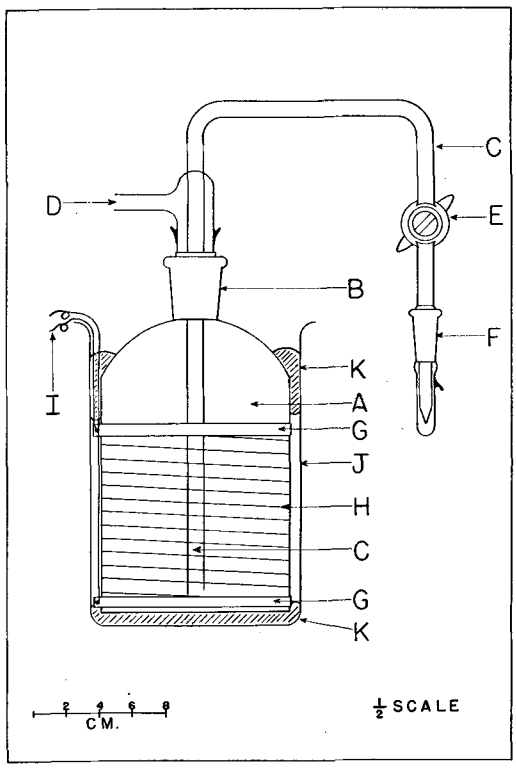


FIG. 3. Reagent dispensing unit.

For the reagent preparation, siphon C is lifted high enough to allow a thermometer to be slipped into neck B, and the oxygen-free nitrogen source is connected to tip F. Variac-controlled heating is then applied to H.

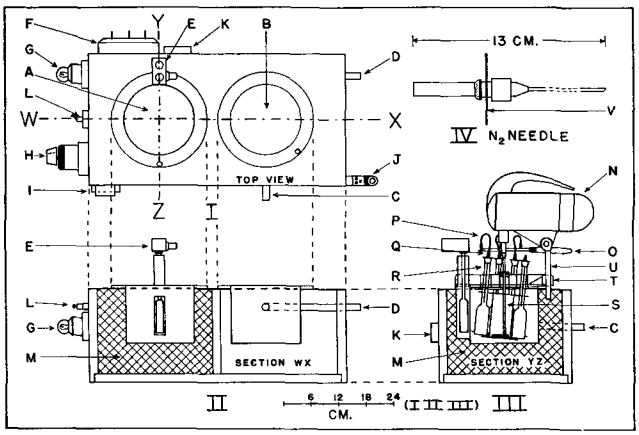


FIG. 4. Isomerization apparatus.

The details of the preparation are those specified in the standard procedure.

The isomerization apparatus proper is shown in Figure 4. In the top view (I) A represents the aluminum heating bath, B the cooling bath of equal diameter and depth. The water leads for the cooling bath are respectively shown as C and D. A De Khotinsky thermoregulator E, pilot light G, relay I, condenser K, and thermoregulator switch L form the elements of a conventional thermoregulating circuit.

A three-position switch H allows the heating element (not shown) to function on low, medium, or high while F allows the current used to be drawn either from the mains or from a Variac transformer connected to the mains.

The parts constituting the heating circuit are fastened at convenient locations to the wooden sides of the box holding the two baths. The latter (Figure 4, II) are supported by their rims from the top of the box. This top is a piece of heat- and chemical-resistant white Arborite. The box is divided into two compartments, the one holding the heating bath being stuffed with glass fiber M for insulation. As section WX shows, the thermoregulator well opens to the inside of the bath.

Section YZ (Figure 4, III) shows, in relation with parts already described, the position of the bottle carrier and driving assembly in the course of operation. Motor N, nitrogen manifold O, bottle rack S, and cover T constitute one whole unit which can be lifted from, or placed in either of the baths when held by the motor handle. The motor is a standard Mix-Master motor, which has proved very convenient. It is fastened to the cover through arm U, fixed in socket T by a set screw. The end of U is used as a plug, which can be slipped in socket J (Figure 4, I). The latter is fastened through a bracket to the top-right corner of the box; it allows the motor and bottle rack unit to be hung in a convenient position for the operation of inserting or removing the bottles.

Figure 4, III shows also how circular nitrogen manifold O, made of brass tubing, is connected by surgical rubber tubing P to needles Q; these needles are prevented from falling into the bottles by light metal disks V (Figure 4, IV).

Figure 4, IV shows the simple construction of a nitrogen needle. The needles used are 19-gauge, 3½-inch Vita lumbar puncture needles, to which a small length of connecting brass tubing has been silver-soldered.

Figure 5 depicts the heating unit in more detail. In the bottom of aluminum bath A is welded the heating element B (Graham No. 623, 1250 W, 3-heat Lo-Lag). The latter is connected to the outside circuit by asbestos-insulated wire, to which it has been silver-soldered. Thermoregulator well C is welded to the side of the bath with which it communicates by a wide port P. That part of C protruding above the bath is cylindrical while the part welded to the bath side is wider and presents a U-shaped cross section.

Three set-screws (not shown), located laterally at the top of C, allow the thermoregulator to be firmly and centrally held in the well.

Cover D is made of ¼-inch aluminum plate. The periphery of the disk is first machined on one face to form a ⅛-inch recess fitting the bath rim. A hole is then bored in the center and a piece of aluminum tubing Q welded on. Q houses ball-bearings G. Two diagonally opposite cut-outs are then made. One is to fit around the protruding end of well C; to the other is welded the set-screw fitted plug H, which is later to receive the motor arm. Six holes are also bored to allow the passage of the bottle necks. A piece of thin-walled tubing, R, is welded to the edge of each hole. The space between tubes is filled with glass fiber and the latter maintained in position by a top cover E, made of thin aluminum sheet stock cut out to match the design of the bottom part. E is fixed by a few spot welds. Finally a light aluminum strip S is welded all round top plate E, thus forming the side of insulated cover D. Direct contact between top and bottom metal surfaces is thus restricted to a few spot welds.

Driving shaft F is fastened to insulated cover D by one fixed (lower) and one adjustable collar as shown.

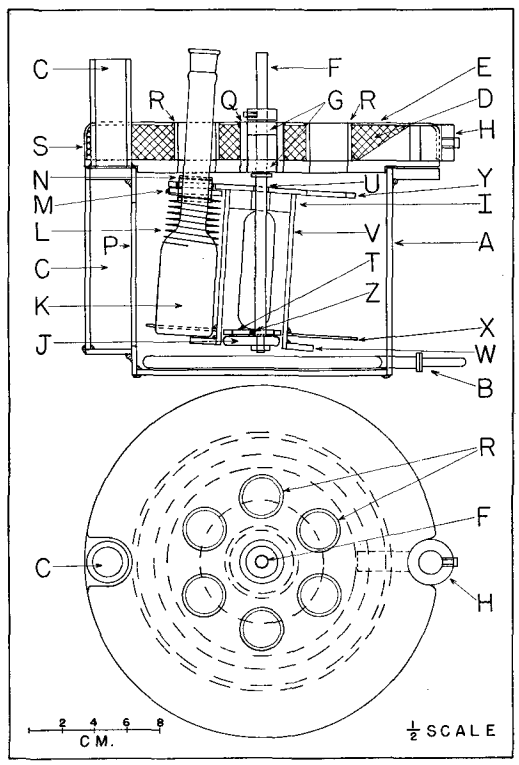


FIG. 5. Details of heating unit.

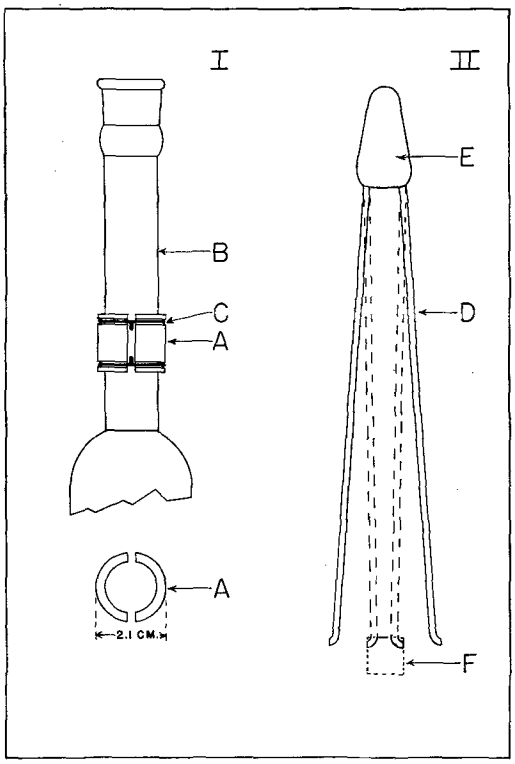


FIG. 6. Bottle fitting and tweezers.

F is linked to the motor by a strong coupling. The other extremity of F is threaded. Brass eccentric J screws on this thread; the lock-nut prevents J from unscrewing when in operation.

Eccentric J supports the bottle rack through collar T. When the machine is in operation, the bottle rack is given a swirling-rocking motion, centered on U. The carrier is prevented from being entrained in a circular motion by the bottle necks leaning on the cover.

When the motor is running and lock-nut is held and prevented from turning, it unscrews immediately. The bottle rack can then be pushed upward just enough to make the eccentric appear. When the latter is unscrewed, the rack can be slipped down and removed. It is then fully accessible and allows the bottles to be inserted or removed as the case may be. Remounting the rack on the shaft is done just as simply.

The carrier rack is constructed from a length of aluminum tubing V, lightened by four oval cut-outs. To the bottom edge is welded a circular shelf W, lightened by multiple perforations.

Just above W is welded a wider circular disk or bottle spacer X, made of thin aluminum sheet stock; this bears six holes, the diameters of which fit the external diameter of the bottles K. The top disk Y of the rack bears corresponding smaller holes and is perforated in its center by hole U; the diameter of U is larger than the shaft diameter to allow for rocking motion of the carrier. A collar M and attached spring L prevent upward motion of the bottle. Lateral motion is prevented by a collar N permanently fastened to the neck of the bottle. N will slide on the neck of the bottle only when pushed. Two diametrically opposed pins Z fasten collar T to the inner wall of V yet allow it to follow the rocking motion.

Inserting a bottle is accomplished as follows. Slip N down on neck, slip ring M and spring L over neck; slip neck through hole in top disk of rack; slip bottle bottom through hole in bottle spacer until it rests on W; push N upwards until it occupies the position shown in Figure 5.

The heating bath is filled with smokeless Dow Corning Silicone fluid 550. When the rack is not immersed, the level is at 60 mm. from the top of the rim. With the rack immersed the spiral of the thermoregulator is completely submerged and the level reaches the necks of the bottles.

Figure 6, I shows the construction of collar N. It is made of a grooved aluminum cylinder A. The latter is sawed lengthwise into two equal parts which are fitted around the bottle neck B and held together by a few turns of chromel wire located in grooves C.

Figure 6, II shows the long tweezers E, made of thick copper wire D, used to slip the cups F containing the samples in the reaction bottles. Tweezers are necessary to avoid splashing. When the cups contain solid fats, this precaution can be omitted.

## Determination of $\Delta$ m

The standard procedure specifies that the cup containing the sample be dropped into the reaction tube containing the hot reagent.

Our kinetic study of the alkali-isomerization reactions, soon to be published, has shown among others, the following facts:

a) The activation energy of all the reactions involved is constant over a wide range of temperature and equal to 27.6 K cal. per mole; the velocity increases 1.08 times for every degree rise in temperature.

b) At 180°C. the reactions involving linolenic acid, for example, are practically completed after 7 minutes; after only 2 minutes about two-thirds of the original material has been transformed. The reaction rates are thus very high. Delayed solution, in such cases, exerts an appreciable distorting effect which renders meaningless, for kinetic purposes, results obtained in this way. The picture is even more complicated by variations due to a human factor since the standard procedure specifies that solution be helped by manual swirling of the reaction tubes. This state of affairs also affects the reproducibility of analytical results.

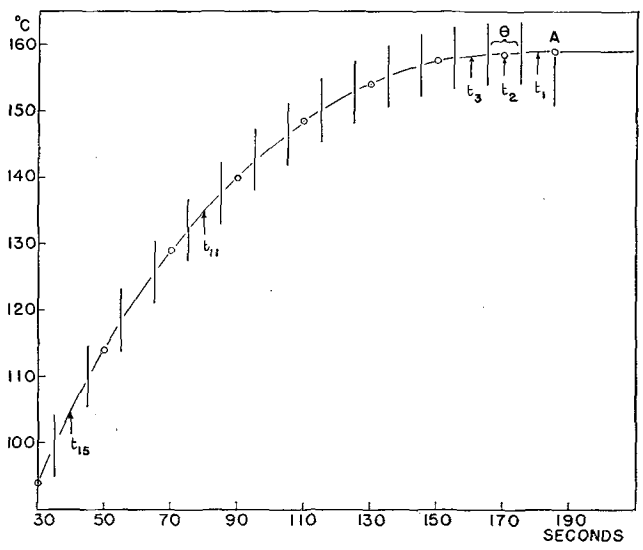


FIG. 7. Reaction mixture heating curve.

In the new procedure the sample is dissolved at any convenient temperature below 100°C. At 80°C., for example, solution is completed for most fatty materials in less than two minutes under the efficient and sustained agitation provided by the apparatus. At the same temperature the reactions are about 1,000 times slower than at 180°C.; no appreciable polyene formation results from this treatment.

The homogeneous reaction mixture is then brought rapidly to R°, the temperature selected as reaction temperature, maintained at R° for m minutes, and then rapidly cooled down to room temperature. In practice, the thermal effects corresponding to the heating up and cooling down phases are appreciable. These effects, in contrast with those resulting from the delayed solution described above, can be easily and quantitatively determined as follows:

Figure 7 represents the time temperature curve of a reaction mixture. In this case R° = 159°C. Point A corresponds to the moment 159°C. has been reached. Let us divide the curve into short equal intervals $\theta$ (here 10 seconds or 1/6 in our time unit), starting from point A down. The temperatures corresponding to the middle of each section $t°_1$, $t°_2$, $t°_3$, ... $t°_n$ are read from the curve. The ratio of the reaction velocity at any of those temperatures to the velocity at 159°C. is

$$f_n = 1.08^{-n}$$
$$\text{with } n = R° - t°_n \qquad (1)$$

Owing to the particular kinetics of the reactions involved, it can be demonstrated that

$$\Delta m = \theta \Sigma_1^n f_n \qquad (2)$$

Where $\Delta$ m is the length of time, expressed in minutes, the reaction mixture would have to be heated at 159°C. to reach the state corresponding to point A. The values of $f_n$ can be obtained from a plot of the function $f_n = 1.08^{-n}$. In our example:

$$\Delta m = 1/6\ (1 + 1 + 0.962 + 0.900 + 0.800 + 0.635 + 0.590 + 0.470 + 0.375 + 0.285 + 0.190 + 0.115 + 0.065 + 0.040)$$
$$\therefore \Delta m = 1.24 \text{ min.}$$

The same procedure is applied to determine the $\Delta$ m corresponding to the cooling phase. It follows that if a specified time M of heating at R° is to be observed, m, the time of heating at R° proper can be adjusted so that

$$M = m + \Delta m$$

The value of $\Delta$ m and consequently the value of m. is accurate under the following conditions:

a) $\theta$ should be small; for all practical purposes $\theta = 10$ seconds is satisfactory.

b) Heating and cooling phases should be short. This can be accomplished, for example, by more rapid agitation or by using bottles made of thinner glass.

c) The time-temperature curve should be established with care; this applies especially to the 15° range below R°.

The advantage of the method lies in the fact that the final result is independent of the conditions under which the operation has been carried out. This eliminates variations due to the human factor as well as those resulting from apparatus characteristics.

The method attains its full practical value when used in conjunction with the new isomerization apparatus. Using this apparatus, it is easy to reproduce a given set of conditions from run to run.

In such cases the variations of $\Delta$ m are small enough to be considered negligible for most purposes.

It follows that the determination of $\Delta$ m need be made only once, and for all, for a given apparatus and a given temperature R°.

## Suggestions for a New Procedure

The complete description of a new procedure should include the specification of the optimum time M, the optimum temperature R°, the corresponding spectroscopic constants, and the set of equations allowing the results to be calculated. This has to await the results of the application of the new method to pure natural acids or esters therefrom. If the old reaction temperature is maintained and a reaction time of 45 minutes is imposed, little change will result in the absorption coefficient for linoleic acid, but an extensive readjustment may affect the absorption coefficient of linolenic and arachidonic acids. Moreover our kinetic study of debromination acids indicates that 180°C. is not the optimum temperature for these two acids.

Meanwhile the description of the new method has to be restricted to the experimental procedure itself. The following is a step-by-step description of a simple and practical protocol of operations. It should be evident from the foregoing that some modifications could be introduced without changing the final results in any way.

The description is divided in Preliminary Steps, which are followed only once and for all, and General Procedure, covering the analytical protocol proper.

*Preliminary Steps*

a) Select for uniform size and weight a series of borosilicate glass Stoddard bottles (see Commercial Standards CS 3-28 of the National Bureau of Standards).

b) Add to each bottle an empty 1-ml. borosilicate glass cup (Cenco 28772, for example). Add exactly 55.00 g. distilled water to each bottle and carefully mark the position of the meniscus.

c) Fit each bottle with a collar N (Figure 6). Make a tare corresponding to 6 g. + the weight of each collar-fitted bottle without stopper. Precision ± 0.01 g. Number flasks and corresponding tares.

d) Take 6 of these bottles. Place one on balance pan, the corresponding tare on the other pan. Equilibrate by adding glycol to the bottle. Repeat with the five others. Insert all six bottles in the isomerization apparatus rack. Fit one of the bottles with a cork which should be equipped with a calibrated thermometer, a nitrogen needle, a sensitive thermocouple, and a slit on the side to allow the nitrogen to escape. Both thermometer bulb and thermocouple junction should be immersed in the liquid. This bottle will become a permanent fixture of the rack. The thermocouple is connected to a calibrated millivoltmeter or to a temperature recorder. The temperature indicated by these instruments will be hereafter called bottle temperature (B.T.).

e) Immerse rack in the heating bath, switch on heater and motor. Adjust speed of the latter to about 250 r.p.m. Note position of the motor dial. The selected speed will never be changed and should be checked occasionally.

f) Find circuit adjustment allowing smooth control of temperature R°. This means both thermoregulator setting and current. Depending on temperature R°, a combination of "low" or "medium" with a particular voltage V as shown by the Variac dial will be found. With this combination the fluctuations of the bottle temperature (B.T.) should not be larger than 0.2°C. at R°. Note this indication V of the Variac dial and the intensity I of the current used for future check. If wide fluctuations of the mains voltage are expected, connect the system to voltage regulator.

g) Find a starting temperature (S.T.). The purpose is to shorten the heating period by immersing the bottles in a bath brought to S.T. $>$ R°. S.T. should be the highest possible temperature of the bath which will not cause B.T. to rise above R° at equilibrium.

Proceed as follows. After the heating current is adjusted for control (V, I), switch off thermoregulating circuit (switch L, Figure 4) and allow the temperature to rise. From time to time stir the oil with a thermometer and note temperature. When the latter has reached a temperature about 10° higher than R°, immerse the rack equipped with all the bottles at room temperature and immediately switch on motor. Then switch on thermoregulating circuit and observe B.T. If, on reaching R°, B.T. does not rise above R° and thermoregulator smoothly takes over control, try higher starting temperatures until the highest possible is found. Note S.T.

h) Repeat the operation starting with S.T. This time start stop watch as soon as rack is immersed. Note B.T. every 20 seconds until R° has been reached. After the bottles have been maintained at R° for a few minutes, switch off motor and immediately lift rack from bath. Let rack rest on edge of bath for 90 seconds; note B.T. every 20 seconds. This step is meant to allow drainage and so cut losses in expensive silicone oil. When 90 seconds have elapsed, immerse rack in cooling bath, start motor immediately, and turn on cooling water stream. Note B.T. every 20 seconds. Calculate global $\Delta$ m from the three time-temperature curves. The specified reaction time being M, deduce

$$m = M - \Delta m$$

Check by repeating operation. Keep note of time at which B.T. reached R° (point A, Figure 7) and of temperature attained at end of 90 seconds drainage period.

The preliminary steps are completed. Keep stoppered and at hand three of the glycol-containing bottles. Analyses should always be conducted with rack fully occupied. The three glycol bottles will be used as dummies to fill unoccupied rack space.

*General Procedure*

a) Start nitrogen train and turn heating on "high."

b) Weigh samples.

c) Equilibrate bottles with corresponding tares by adding required amount of reagent $\pm$ one drop. Each time a bottle is supplied with reagent, introduce cup containing sample using tweezers and slip tube leading nitrogen into neck. Add reagent to next bottle. When this is ready, stopper first bottle and slip nitrogen tube in next. Proceed in this way until all bottles are supplied. An empty cup is added to the blank bottle.

d) Switch nitrogen stream to manifold and place bottles in rack. Fill empty spaces with dummies. Slip nitrogen needles in bottle necks and keep flow at 300 cc./minute for five minutes.

(At this point it is possible with most fatty materials to pass directly to the next step (isomerization proper) because complete solution in the reagent will occur during the early stages of heating while the temperature of the reaction mixture is still under 100°C. For others however, the solid fats in particular, the following intermediate steps should be included: fill bath B with hot water, immerse the bottle-laden rack, and switch on motor; when solution is complete, turn on cold water to bring to room temperature.)

e) The temperature in the bath should now be near or have attained R°. Switch off thermoregulating circuit and set current at control value I. Let temperature rise to S.T. At last stages stir bath with thermometer. When S.T. is attained, introduce rack in bath, start motor and stop watch; switch on thermoregulating circuit.

f) Shortly after, reduce nitrogen flow to 160 cc./minute (30 cc./min./bottle). Observe B.T. and note time B.T. reaches R°. Let reaction proceed at R° for m minutes.

g) After this time has elapsed, stop motor, lift rack from bath, and let it rest on edge for 90 seconds. Note B.T. at end of period.

h) Immerse rack immediately in cooling bath and start motor. Turn on cooling water stream. Increase nitrogen flow to 300 cc./min. Wait 5 minutes.

i) Stop motor, lift rack from bath, hang rack to bracket J (Figure 4). Wipe bottles and rack with tissue paper, remove needles and stopper bottles one by one, remove rack and remove bottles from rack.

j) To one of the bottles add about 40 ml. 95% ethyl alcohol, slip nitrogen tube in neck; wait about one minute, stopper, and proceed similarly with all bottles. Shake all bottles vigorously. Examine from time to time for complete solution of reaction mixture and complete flocculation of silicates. Use shaking machine if available.

k) Make up to the 55-ml. mark, with 95% ethyl alcohol, stopper and homogenize contents of each bottle. Centrifuge about 40 ml. from each bottle in nitrogen-filled, stoppered centrifuge bottles. Use angle centrifuge at moderate speed (1,500 r.p.m.) for 15 to 20 minutes. At the end of this period the precipitate sticks to the bottom, leaving perfectly clear supernate.

l) Use clear liquid for further dilutions and proceed as specified by the standard method.

## Experimental Results

Table I shows a series of results obtained with pure methyl linoleate and linolenate (no corrections needed). They are truly representative of a larger set of results (over 350) which have been obtained through the procedure just described. They have been

TABLE I

Alkali Isomerization of Debromination Methyl Linoleate and Methyl Linolenate
(6.5% KOH-Glycol for Time and at Temperature Indicated)
Sp.*a*, 1 cm., 1 g. per 1000 ml. at Indicated Wave Lengths

| Conditions | Bottle A | Bottle B | $\Delta$ B | Run Average | $\Delta$ R | Material | Mean $\Delta$ B | Mean $\Delta$ R |
|---|---|---|---|---|---|---|---|---|
| | Sp.*a* | Sp.*a* | | Sp.*a* | | | | |
| 20 min.<br>149°C.<br>$\lambda$ = 233 m$\mu$ | 26.86<br>26.70 | 26.55<br>26.65 | +0.30<br>+0.05 | 26.70<br>26.68 | +0.01<br>+0.01 | Methyl Linoleate | +0.18 | 0.01 |
| 60 min.<br>149°C.<br>$\lambda$ = 233 m$\mu$ | 57.20<br>56.80<br>57.20<br>57.40<br>57.70<br>57.25 | 57.20<br>56.55<br>56.75<br>56.50<br>57.50<br>57.15 | +0.00<br>+0.25<br>+0.45<br>+0.90<br>+0.20<br>+0.10 | 57.20<br>56.67<br>57.00<br>56.95<br>57.60<br>57.20 | +0.10<br>−0.43<br>−0.10<br>−0.05<br>+0.60<br>+0.10 | Methyl Linoleate | +0.3 | 0.2 |
| 40 min.<br>164°C.<br>$\lambda$ = 233 m$\mu$ | 77.10<br>77.60<br>77.35<br>77.95 | 76.55<br>76.70<br>lost<br>77.10 | +0.55<br>+0.90<br>.....<br>+0.85 | 76.83<br>77.15<br>77.35<br>77.53 | −0.45<br>−0.13<br>+0.07<br>+0.25 | Methyl Linoleate | +0.75 | 0.225 |
| 80 min.<br>129°C.<br>$\lambda$ = 233 m$\mu$ | 47.80<br>47.55 | 48.00<br>48.20 | −0.20<br>−0.65 | 47.90<br>47.88 | +0.01<br>−0.01 | Methyl Linolenate | −0.43 | 0.01 |
| 80 min.<br>129°C.<br>$\lambda$ = 268 m$\mu$ | 35.40<br>35.65 | 35.80<br>35.70 | −0.40<br>−0.05 | 35.60<br>35.67 | −0.035<br>+0.035 | Methyl Linolenate | −0.23 | 0.035 |

selected from those corresponding to a rising portion of the time-absorption coefficient curves. Results corresponding to the flat, post-maximum portion of the curves present appreciably smaller deviations as would be expected.

The results are shown listed in pairs, each pair representing duplicate analyses performed in the course of the same run; Δ B shows the difference between the result obtained using bottle A and that obtained using bottle B. All determinations involving methyl linoleate were carried out using the same pair of bottles. A different pair was used for methyl linolenate. The values listed under Δ R represent the deviation of the run average (average of twin duplicates) from the average value for the complete series of duplicates.

It must be pointed out that the supply of freshly prepared esters was kept in several 1-g. evacuated ampoules and in the cold. For more immediate use one ampoule would be opened and its contents stored in a tight-fitting hypodermic syringe equipped with a long fine needle. Between deliveries the stylet supplied with the needle was kept in the latter. This procedure was found more practical and safer than keeping the supply under nitrogen. The specific absorption coefficient of esters kept under nitrogen showed an appreciable change over a period of two weeks, due presumably to the cumulative effect of short periods of exposure to oxygen occurring every time the container was opened for the withdrawal of a sample and despite the fact that the blanket of nitrogen was renewed immediately after the weighing. No change was observed after two weeks when a syringe was used.

## Discussion

The consistency of the sign affecting Δ B shows a definite difference in bottle characteristics. The relative importance of mean Δ B against mean Δ R suggests that these differences play an important role and that more consistent results could be obtained if bottles of more uniform characteristics were used.

As they are, the results show a definite improvement over those obtained by the old procedure. As mentioned above, Δ B is much smaller among results corresponding to the flatter portion of the time-absorption coefficient curves; the deviations of Δ R are also smaller, although to a lesser degree. The standard Δ R deviation for such results is about 0.3%. This low standard deviation is proof of the reproducibility of conditions from run to run obtainable through this procedure. The proof for the validity of the Δ m procedure was found in the homogeneity of results obtained over a wide range of temperatures and times, all of which fitted the same simple kinetic pattern.

The wet deoxygenator described above is an adapted version of the apparatus proposed by Uhrig *et al.* (3) for oxygen determination in hydrocarbons. It is more efficient than the furnace used in the standard procedure. The presence of oxygen in the blanketing nitrogen has long been recognized as a source of error. Intrusion of oxygen into the bottles can readily be detected, unfortunately after treatment, by the browning of the normally colorless bottle contents.

Note the comparatively much smaller amount of nitrogen used for blanketing each bottle (30 cc. against 50 to 100 in the standard method). The reason for this lies in the use of long-necked bottles instead of the wide tubes as in the standard method. Better and more uniform nitrogen distribution is ensured by the use of standard-gauge nitrogen needles instead of the arrangement formerly proposed. The needles are also more practical leads than the fragile glass ones used hitherto.

The advantages of the Stoddard bottles are not limited to efficiency in nitrogen blanketing. The T stoppered, narrow, graduated neck allows the first dilution of the reaction mixture to be effected in the reaction bottle itself and so eliminates the oxidation hazard of the otherwise cumbersome transfer described by the old procedure. Further the flat bottom of the Stoddard bottle promotes efficient stirring and offers a large heating area.

The elimination of specially purified absolute alcohol introduces, it is true, an extra step of centrifugation. The work involved is not considerable however and is easily compensated by the elimination of manipulations and expense involved in the preparation of the former type of solvent.

Note also the reduction in the quantity of reagent used (6.00 g. instead of 11.0 g.) which is ultimately a time and labor saving modification. The apparatus described for handling the reagent allows the latter to be prepared, stored, and dispensed under continuous protection. In combination with a torsion balance it constitutes a practical unit allowing a fast and clean weighing operation. In relation to reagent handling it should be pointed out that accurate weighing is unnecessary for routine analytical work. The authors found that filling to a predetermined mark corresponding to the volume of 6 g. reagent was sufficiently accurate. They observed that up to 1.5 g. excess reagent in a sample bottle, while the blank bottle contained the normal amount, did not affect appreciably the results corresponding to the flat, post-maximum region of the time-absorption curves. For samples leading to very small absorption values or for kinetic work, the reagent has to be measured more accurately.

Simultaneous treatment of all samples and blanks not only eliminates an important source of error, but appreciably facilitates the operator's task.

To summarize, the new procedure represents an improvement in accuracy, practicality, and reliability.

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