

Esterification Rates of Fatty Acids with Methanol

IN A RECENT PAPER ON "Preparation of Partial Glycerides by Direct Esterification" (1) Gros and Feuge report a considerable difference between the esterification rates of saturated acids such as lauric and stearic and the unsaturated oleic acid with glycerol. Thus after 6 hours' reaction in acetonitrile solution at 100C the wt% of esterified acids was 81.4 for lauric, 82.2 for stearic and 33.6 for oleic. They state that their results are in agreement with the data published in "International Critical Tables" (2). The data in question refer to esterification rates of various organic acids in methanol catalysed by HCl and expressed as monomolecular constants K at 15C for $[HCl] = 1$. The values for fatty acids were compiled from two early papers by Sudborough and Gittins (3,4). However, the comparison of these values with those appearing in the original publications has revealed some startling discrepancies as may be seen in Table I.

It would seem that the compiler has multiplied the results in Sudborough and Gittins' first paper by a factor of 2.303, presumably to convert decimal logarithms into natural ones—an operation sometimes wrongly omitted in the calculation of reaction rates.

TABLE I

Comparison Between the Monomolecular Constants K at 15C for Catalysed Esterification of Fatty Acids in Methanol Reported in "International Critical Tables" and in Original Publications

Acids	International critical tables	Sudborough and Gittins (3)
Formic.....	2568	1124
Acetic.....	239	104
Propionic.....	211.7	91.9
n-Butyric.....	115.2	50.0
n-Valeric.....	123.2	53.5
Caproic.....	118.7	51.5
n-Heptylic.....	120.9	52.5
Caprylic.....	125.8	54.6
n-Nonylic.....	123.5	53.6
Capric.....	119.3	51.8
Lauric.....	121.9	52.9
Myristic.....	120.9	52.5
Palmitic.....	114.4	49.7
Stearic.....	123.7	53.7
Undecylenic.....	53.0	52.5
Oleic.....	54.4	54.3
Elaidic.....	54.4	54.3
Erucic.....	51.2	52.3
Brassicidic.....	51.8	51.6

Sudborough and Gittins (4)

He did it without noticing that Sudborough and Gittins had already—and quite conspicuously—applied this factor. The values for unsaturated acids obtained from Sudborough and Gittins' second paper escaped the above-mentioned unwarranted correction. As a result the rates for unsaturated acids shown in "International Critical Tables" are much lower than those for saturated acids. This is contrary to Sudborough and Gittins' results and their explicit statement that with the exception of the three lowest members the esterification rates of saturated and unsaturated fatty acids in methanol are, irrespective of molecular weight, on the whole, similar, provided the double bond is further than in the 3,4 position. Incidentally, measurements carried out in this laboratory have confirmed that esterification rates of lauric, oleic, elaidic and linoleic acids in methanol containing 0.007 moles HCl/liter are practically the same.

The above facts do not necessarily invalidate Gros and Feuge's results obtained in the esterification of stearic and oleic acids with glycerol and under different experimental conditions. In fact, the *cis*-configuration of oleic acid is conducive to steric hindrance if glycerol is the esterifying agent, and the difficulty of introducing the oleic acid radical into diglycerides at room temperature is well known. Nevertheless the great difference in the esterification rates of stearic and oleic acids at 100C when using a large excess of glycerol is rather unexpected.

There are some further inaccuracies in the particular table of "International Critical Tables" previously referred to, which can not be readily explained. However, they pertain to acids other than aliphatic and thus are outside the scope of the present communication.

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• Addendum

JAOCS **42**, pages 344-345, April 1965, A. Vioque et al.: Trace Elements in Edible Fats. IX. Influence of Demetalization on the Oxidative and Flavor Stabilities of Soybean Oil. Table IV should appear as follows (note particularly the 5, 9, and 10-hour figures):

TABLE IV
Change of Tocopherol and Peroxides in AOM Test of Original and Demetalized Oils

Treatment	Original oil 837		Demetalized oil 837	
	Tocopherol $\mu\text{g/g}$ 1300	Peroxides meq/kg 14.7	Tocopherol $\mu\text{g/g}$ 1240	Peroxides meq/kg 12.5
Crude refining and deodorization.....	860	0	1080	0
A.O.M.— 5 hr.....	420	50	720	45
6 hr.....	280	60	520	55
7 hr.....	180	75	475	65
8 hr.....	50	95	280	80
9 hr.....	5	180	235	88
10 hr.....	3	460	15	150