Effect of Temperature on the Twitchell Fat Splitting Process and Its Catalysts

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IN a paper on industrial fat splitting, published recently in this Journal, L. Lascaray (3) raised several questions of both theoretical and practical importance. There is little doubt that, owing to his investigations (4) over the last 15 years, fat hydrolysis by the autoclave and Twitchell processes has been recognized as an essentially homogeneous reaction which takes place in the oil phase, being sustained by water dissolved in this phase. At the same time it is quite natural that Lascaray's latest interesting study should contain several controversial points, and the following remarks are meant to deal with a few of them as far as they relate to the Twitchell process.

Kinetics of Fat Hydrolysis

Lascaray's views on the mechanism of fat-splitting have received support from the kinetic study of the acidification method by Suen and Chien (5) and more recently from the work of the present writer (2), who, on obtaining a consistent first-rate kinetic order for the Twitchell hydrolysis, concluded that this order can be explained in the simplest way on the basis of a homogeneous reaction in the oil phase. Commenting on these investigations, Lascaray states (3) that the rate of fat-splitting is governed principally by the physical process of diffusion of water into the fat (and of glycerol into water), which is slower than the chemical process of hydrolysis. Since the diffusion equation has a mathematical form similar to that of a unimolecular reaction, an apparent first order rate is bound to be observed in any case and has no bearing on the reaction velocity of the hydrolysis proper. Only after establishing the temperature coefficients of the reaction rate for a given method of fat splitting (*i.e.*, factors expressing the relative increase of reaction velocity on raising the temperature by 10°C.) could one deduce whether the observed rates represent the kinetics of diffusion or of hydrolysis. If diffusion were the rate determining factor, the temperature coefficients would be 1.2-1.5; and coefficients of a similar order were found by Lascaray in the autoclave process between 150°C. and 220°C.; if however the rate were governed by hydrolysis, the latter being a homogeneous chemical reaction, one would expect temperature coefficients of 2 or more.

Lascaray's postulates, as outlined above, appear perfectly reasonable, and it so happens that the temperature coefficients of the Twitchell process can be computed from the equation $\log_{10} k = 9.802 - 3885/T$ given recently by Cox (1), where k is the velocity constant and T the absolute temperature.[1] This equation has been derived from a series of Twitchell trials carried over the range from 60°-100°C. with subsequent extrapolation to 150°C. Temperature coefficients calculated from it by the present writer appear in Table I. It will be seen that around 100°C., which is the temperature used in the Twitchell process, they are approximately 2 and diminish as the temperature approaches 150°C., a fact which could be attributed to the limiting influence of diffusion on the reaction velocity. For processes carried out at 100°C., such as Twitchell and possibly also acidification processes, the kinetic order observed would therefore, according to Lascaray's own postulate, pertain to the chemical reaction of hydrolysis rather than to the physical phenomenon of diffusion. Incidentally, temperature coefficients found by Lascaray (3) in the autoclave process between 100°C. and 150°C. appear to be on the average also of the order of 2 for each 10°C., the relative velocity factors at 100°C. and 150°C. being 0.03 and 1, respectively. This would indicate that, independent of the method used, the fat hydrolysis near 100°C. is a reaction slow enough not to be hampered by diffusion.

TABLE I

Temperature Coefficients of the Twitchell Hydrolysis[a]

Temperature °C.	Velocity constants k	Temperature coefficients k_{t+10}/k_t
60	0.0135	.....
70	0.0303	2.24
80	0.0619	2.04
90	0.126	2.04
100	0.241	1.91
110	0.459	1.91
120	0.824	1.79
130	1.452	1.76
140	2.489	1.71
150	4.140	1.66

[a] Calculated from the equation $\log_{10} k = 9.802 - 3885/T$ established experimentally by C. B. Cox (1).

Twitchell Hydrolysis at Temperature Exceeding 100°C.

In view of the slow rate of the Twitchell hydrolysis at 100°C. Cox in his previously mentioned study (1) arrived at the interesting conclusion that there is nothing to be gained from replacing the customary batch countercurrent system by a continuous process of splitting in stages. For the same output the size of the vessels required in the latter process would be larger than in the batch system. On the other hand, a great saving of time and steam consumption would result from carrying the Twitchell process above 100°C., which would mean in practice the applying of moderate pressures. Such a process was patented a number of years ago (6), but since, according to Lascaray, Twitchell catalysts are destroyed at elevated temperatures, it appeared of interest to find, experimentally, the temperature to which these catalysts can be subjected without impairing their efficiency.

Two kinds of catalysts were tried: the "Kontakt" type (petroleum sulphonic acids) and the old Twitchell reagent (crude sulpho-aryl-stearic acids). Both

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[1] The excellent and comprehensive paper on the Twitchell process by C. B. Cox appeared in the Transactions of the Institution of Chemical Engineers (London) under the date of 1949, but as the volume in question was not published before the end of 1951, I had unfortunately no knowledge of it when carrying out my own investigations of the Twitchell hydrolysis in 1950.

reagents were made into 2% aqueous solutions containing 2% sulphuric acid and held in covered beakers for 3 hours at 150°C. and 180°C. in gas-heated laboratory autoclaves charged with a little water. The aqueous suspensions of the reagents so treated were used for splitting tallow at 100°C. and 150°C., applying in each case 1% reagent, 1% sulphuric acid, and 100% water calculated on the fat basis.

Parallel tests were run with reagents not subjected to previous heating. Some typical results are shown in Table II and indicate that the preheating of the old type of Twitchell reagent to 150°C. (approximately 55 lb. per square inch pressure) impaired to some extent its performance in the subsequent hydrolysis of tallow at 100°C. whereas the "Kontakt" reagent remained unaffected. Preheating to 180°C. reduced the efficiency of both reagent types quite distinctly. At 150°C. however hydrolysis was practically completed in 3 hours, both with previously heated and unheated reagents, a circumstance which denotes a remarkably short reaction time considering that no stirring was applied. The use of 0.5% ZnO as a catalyst gave under similar conditions a 34% split as compared with 90% achieved with Twitchell catalysts. When the sweet water from the Twitchell hydrolysis was removed and 50% of fresh water and 0.5% sulphuric acid but no more reagent was added to the fat, a further hour of heating at 150°C. yielded a 96% split. These results were obtained independent of the type of Twitchell reagent employed. The chief obstacle against replacing basic catalysts in the autoclave process with Twitchell reagents appears therefore to be the corrosive action of diluted sulphuric acid on metals used in the construction of autoclaves. Despite statements to the contrary a small amount of this acid seems to be essential for satisfactory working of the Twitchell reagents, and even if free sulphonic acids only were used, their corrosive action on metals would also lead to difficulties. Nevertheless the advantages of a Twitchell process carried out under moderate pressures seem so evident that one can only wish for an early solution of the problem of finding a sufficiently resistant material. This would at the same time facilitate the developing of a continuous Twitchell process.

TABLE II

Effect of Temperature on Twitchell Catalysts (Kontakt Reagent Denoted "A" and Twitchell Reagent "B")

Materials: Tallow with 5.5% F.F.A.; 1% catalyst; 1% H_2SO_4; 100% H_2O

Time	Splitting Degree, %									
	Hydrolysis at 100°C. with catalysts						Hydrolysis at 150°C. with catalysts			
	Preheated to 180°C. 3 hours		Preheated to 150°C. 3 hours		Untreated		Preheated to 150°C. 3 hours		Untreated	
	"A"	"B"	"A"	"B"	"A"	"B"	"A"	"B"	"A"	"B"
hours										
3	22	6	40	6	41	6	92	91	92	90
6	46	9	62	10	61	10				
12	53	42	71	50	71	58				
18	75	61	85	70	85	82				
24	75	65	88	77	88	82				

Summary

Velocity constants of the Twitchell hydrolysis have been calculated from recently published experimental data and found to increase approximately twofold for a 10°C. rise around the temperature of 100°C. This seems to indicate that the rate of reaction is governed by hydrolysis rather than by diffusion of water into the fat phase (and of glycerol into water).

Preheating to 150°C. reduces the efficiency of the old type of Twitchell catalyst but does not affect the "Kontakt" reagent. The increasing of the temperatures from 100°C. to 150°C. substantially accelerates the hydrolysis independent of the type of Twitchell reagent employed.

Acknowledgment

The author is indebted to Miss H. E. Watt for technical assistance.

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[Received December 29, 1952]

The Chemical Utilization of Fats and Oils. II. A New Reaction of Glycerides

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THE usual method of preparing aralkyl ketones consists of the condensation of acids, acid chlorides, or acid anhydrides with aromatics in the presence of a catalyst such as aluminum chloride. This paper describes the direct condensation of glycerides with benzene to give aralkyl ketones in yields comparable with those obtained by conventional means.

Experimental

The aluminum chloride-catalyzed condensation was accomplished as follows (Table I): The glyceride was dissolved in a large excess of benzene. About one-third of the aluminum chloride to be used was added portion-wise during the first half-hour on the steam bath, and the balance of the catalyst was introduced thereafter. The mixture was shaken vigorously at frequent intervals during the reaction period. After standing overnight, it was drowned in ice water acidified with hydrochloric acid. The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic portions were washed with water and dried. The ketones were isolated by distillation.