well-known breakfast food, puffed rice. The tedious grinding in the pebble mill can thus be avoided.

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THE RATE OF HYDROGENATION OF ACETOACETIC ESTER, DEHYDROACETIC ACID, BENZENE, PHENOL AND ANILINE OVER NICKEL AT PRESSURES FROM 27 TO 350 ATMOSPHERES

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There appears to be comparatively little information available as to the relation of the pressure of hydrogen to the rate of hydrogenation of liquids with nickel catalysts. Ipatiev believed that pressures of the order of a hundred atmospheres were advantageous, while others have been but little impressed by the advantages of such pressures.[1] The experimental work described in this paper was performed in order to find out, in the case of a few supposedly representative compounds, what pressures could most advantageously be used for their hydrogenation.

The disadvantages in the use of pressures above a few atmospheres are obvious. Glass apparatus and rubber tubing may not be used, so that the assistance of a mechanic and materials often not available in the laboratory are required for the construction of the apparatus. The advantages in the use of pressures up to 80 or 150 atmospheres are no less real. Pressures of these magnitudes raise the boiling points of all organic materials which are liquids under laboratory conditions to 190° or above. This makes it possible to use any of the common solvents and to subject in the liquid phase almost all organic compounds to the action of hydrogen and the nickel catalyst. It also makes it possible to store in the reduction chamber a much greater quantity of hydrogen and thus avoid any auxiliary tank such as is necessary in reduction of pressures of a few atmospheres. This makes it possible to use a very simple set-up which includes only one inexpensive valve of the type designed for holding pressure on but one side. (Such an apparatus is manufactured by the Burgess–Parr Co. of Moline, Ill.) At least for small-scale operation in the laboratory the advantages of using pressures in the range 60 to 120 or 150 atmospheres as compared with pressures below perhaps 5 atmospheres seem to be

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[1] Sabatier and Reid, "Catalysis in Organic Chemistry," D. Van Nostrand Co., New York, 1922, p. 207.

quite considerable with no material increase in danger, inconvenience or expense. The use of pressures materially higher than these necessitates additional and more expensive equipment, for hydrogen is usually purchased in tanks holding the gas under a pressure of about 125 atmospheres. A bomb filled at this pressure and heated to 200°, which may be regarded as a reasonable upper limit necessary for operation with a nickel catalyst, would show a pressure of about 190 atmospheres. This represents then the maximum pressure which may be obtained without considerable additional equipment.

Acetoacetic ester, dehydroacetic acid, benzene, aniline and phenol were selected as representative compounds for testing out the practical advantages of various pressures up to 350 atmospheres. Acetoacetic ester and benzene absorbed one mole and three moles of hydrogen, respectively, while phenol and aniline were not completely reduced under the conditions selected, the ratio of catalyst to reactant and the temperature being too low for complete reduction. These compounds were completely reduced if a higher ratio of catalyst or temperature was used. In so far as our experience goes dehydroacetic acid requires a second or third application of catalyst in order to obtain complete reduction. "Complete reduction" in the two lower ranges of pressure means three moles of hydro-

TABLE I

THE RATE OF REDUCTION OF ACETOACETIC ESTER, BENZENE, PHENOL AND ANILINE AT VARIOUS PRESSURES

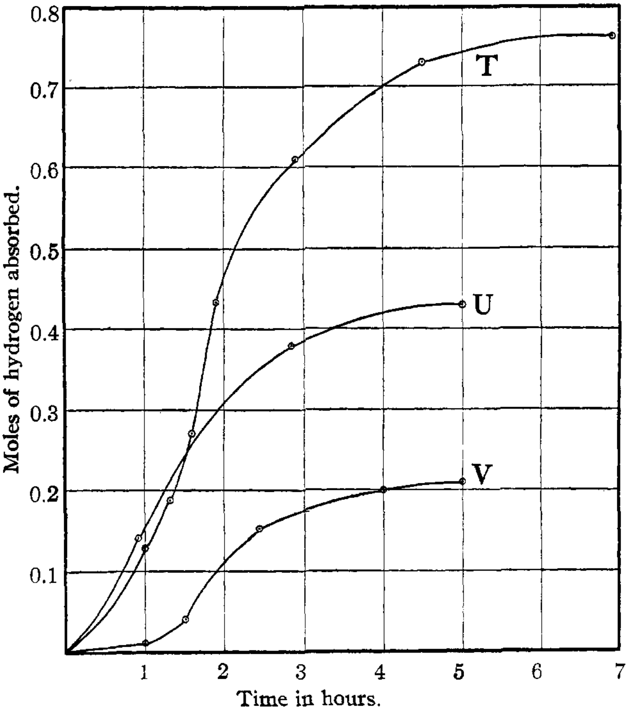
Time, hrs.	% of acetoacetic ester hydrogenated (a)			% of benzene hydrogenated (b)		
	27 ± 13 atm.	122 ± 13 atm.	350 ± 6 atm.	30 ± 17 atm.	169 ± 19 atm.	323 ± 17 atm.
0	21	36	83	17	29	34
0.5	40	62	100	40	68	75
1.0	55	76		61	90	93
1.5	72	85		76	98	100
2.0	86	91		87	100	
2.5		95		96		
3.0	97	98		100		

Time, hrs.	% of aniline hydrogenated (c)			% of phenol hydrogenated (d)		
	34 ± 14 atm.	190 ± 20 atm.	340 ± 15 atm.	40 ± 20 atm.	150 ± 26 atm.	330 ± 15 atm.
0	4	17	15	5	13	20
1	9	34	36	27	49	49
2	13	44	49	41	63	62
3	17	51	59	50	73	70
4	21	56	64	59	81	
5	25	62	70	67	85	
6	29	65	75	72	87	
7	32	68		76		

(a) 0.39 mole of acetoacetic ester with 2 g. of catalyst at 150°. (b) 0.16 mole of benzene with 1 g. of catalyst at 120°. (c) 0.33 mole of aniline in 50 ml. of methyl cyclohexane with 2 g. of catalyst at 175°. (d) 0.33 mole of phenol with 1 g. of catalyst at 120°.

gen per mole of dehydroacetic acid, while at the higher pressure it means five moles of hydrogen per mole of acid. The products formed in the hydrogenation of acetoacetic ester and dehydroacetic acid have been considered in an earlier paper.[2]

There is shown in Fig. 1 the effect of increased pressure upon the rate and extent of absorption of hydrogen by dehydroacetic acid. The data given in Table I show the rate of progress toward complete reduction at different pressures for acetoacetic ester, benzene, phenol and aniline. Zero time was taken as the time at which the thermocouple in the bomb first showed the temperature which had been selected for allowing the reaction to proceed. The figures given in the tables are for individual experiments which have been duplicated at least once. The general effects have been observed in numerous experiments. The duplicate experiments showed



T, 323 atm.; U, 149 atm.; V, 108 atm.

Fig. 1.—The rate of absorption of hydrogen by dehydroacetic acid at various pressures. The moles of hydrogen absorbed at three pressures are plotted against the time in hours for the reduction of 50 g. (0.3 mole) of dehydroacetic acid in 100 ml. of methylcyclohexane, using 4 g. of a nickel catalyst at 185–190°.

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[2] Adkins, Connor and Cramer, This Journal, **52**, 5192 (1930).

no variation greater than 3% from the values reported in the tables. The experimental methods, catalysts, etc., were those described in a recent paper.[3] It must be pointed out that in measuring the rate of reduction, the absorption of hydrogen at a given time must necessarily be calculated from measurements of pressure at the temperature of reduction. This presents no particular difficulties in measuring the rate of reduction of compounds which are quantitatively reduced under the experimental conditions, for the final drop in pressure at the temperature of reduction represents 100% reduction and the percentage reduction at various times may be simply and accurately calculated. If the compound under consideration is not completely reduced, then the drop in pressure must be evaluated in terms of the standardization figures for the apparatus determined for some other compound such as acetone which is quantitatively reduced. At the higher pressures and temperatures the results so obtained are less accurate than at lower pressure.

Summary

The relationship of pressure to the rate of catalysis by nickel of the hydrogenation of acetoacetic ester, dehydroacetic acid, benzene, phenol and aniline has been found to differ greatly among these five compounds. It was entirely feasible to reduce acetoacetic ester at pressures in the vicinity of 30 atmospheres but the rate of reduction was greatly increased by increases in pressure, especially in the range from 120 to 350 atmospheres. Dehydroacetic acid reduced more than twice as rapidly at 149 as at 108 atmospheres and about four times as rapidly at 323 as at 108 atmospheres. It was found impractical to reduce aniline in the 30 atmosphere range. Increasing the pressure greatly increased the rate of hydrogenation, but increasing the pressure in the higher ranges up to 350 atmospheres was not found to be particularly advantageous. The rate of reduction of phenol and of benzene proceeded well in the 30 to 40 atmosphere range, increased with pressure to the 150 to 170 atmosphere range but was not sensitive to further increase in pressure up to 330 atmospheres.

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[3] Adkins and Cramer, THIS JOURNAL, 52, 4349 (1930).