are rate limiting processes [3] was applied to kinetic data for the initial rates (no influence of products) of the dehydrogenation of sec-butyl alcohol over a brass catalyst.[4] This reaction had previously been shown to deviate from the behaviour predicted by the Hougen model, and it seemed necessary to assume a transition from one rate controlling step to another with increasing temperature.[4,5] The kinetic data may be explained in a different way, however, which has surprisingly been overlooked so far, when interpreting kinetic results in catalysis. A preliminary account is given here.

The kinetic equations of Hougen and Watson [2] are based on the assumption that there is only one type of active sites. Hence for a surface reaction controlled mechanism involving n centers we have at zero conversion

$$r = \frac{k\,a\,p}{(1 + ap)^n} \qquad (1)$$

where r is the reaction rate (moles per second, and mass or surface unit of catalyst). k is the rate constant and a is an adsorption constant. Several reasons may be advocated for assuming that in general there are two or more sets of active centers. These reasons will not be given here, but if we do assume the catalyst to consist of two different sets of centers, eqn. 1 is transformed into

$$r = \frac{k_1\,a_1\,p}{(1 + a_1p)^n} + \frac{k_2\,a_2\,p}{(1 + a_2p)^n} \qquad (2)$$

Applying eqn. 2 to the set of data given by Thaller and Thodos [4] for $t = 600°F$ by carrying out a least squares parameter estimation an excellent fit is obtained. Choosing $n = 3$, one obtains parameter estimates, $k_1 = 0.1805$, $a_1 = 1.2671$, $k_2 = 0.2646$, $a_2 = 0.1017$ and a mean percentage deviation of 2.53 % corresponding to 4.31 % per degree of freedom. The mean residual square per degree of freedom is 2.342×10^{-6}.

This mean residual square is probably not larger than the experimental variance, thus the bias of the curve may be zero. Eqn. 2 may therefore possibly give a complete description of the reaction, although lack of bias does not imply correctness of the model and a bias may occur in other experimental regions of the system. When appropriate, all other kinetic equations of the Hougen type may of course be transformed into sums in analogy with the transformation of eqn. 1 into eqn. 2.

A complete description of the work will appear shortly.

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Influence of γ-Irradiation on β-Fructofuranosidase in Potato Tubers

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As early as 1903 Kastle and Clark [1] detected β-fructofuranosidase ("invertase") in potato tubers. These authors reported that "invertase" was found only in sprouted, but not in unsprouted, tubers, an observation later confirmed also by McCready.[2]

Denny *et al.*[3] found that the "invertase" activity of potato juice from tubers treated with a sprout inhibitor was greater than that from the juice of untreated tubers. The sprouting of the tubers is irreversibly inhibited by suitable doses of γ-irradiation; thus, it seems obvious to assume that the activity of the "invertase" in the tubers would be influenced also by irradiation.

In order to investigate whether this hypothesis could be confirmed, crude "invertase" preparations were isolated from irradiated and non-irradiated potato tubers, and enzyme activities of these preparations were determined.

Experimental. Potato tubers of the varieties King Edward and Bintje were used for this investigation. "Invertase" was isolated from freshly harvested control tubers and from those stored for one year. Tubers were irradiated at different intervals after harvest, as described earlier,[4] and used for the enzyme isolation immediately after irradiation or after a storage time of one year. The isolation of the enzyme and the determination of the activity was performed partly according to Schwimmer *et al.*,[5] partly according to the following modification of the method described in Ref. 5: 50 g of peeled potatoes were rapidly cut in pieces and blended in a Waring Blendor with 25 mg ascorbic acid. The slurry was pressed through cheese-cloth in a special press with high pressure capacity (4000 kg/cm²). The press-juice was centrifuged twice at about 500 *g* to remove cell debris and starch. The supernatant was used for the determination of "invertase" activity. The temperature was maintained at 0–2°C during the isolation procedure. The enzyme activity was determined at 30°C in the reaction mixtures as follows:

A. 6.4×10^{-2} M sucrose and 5×10^{-3} M sodium acetate buffer at pH 4.4 (final concentrations), and 0.25, 0.5, or 1.0 ml enzyme solution in a total volume of 7 ml. The action of the enzyme was terminated by placing the sample withdrawn in ice-water and adding cation exchange resin Amberlite IR-120 (H). After 10 min anion exchange resin Amberlite IR-4 (OH) was added. The sample was kept at 0°C for one h, diluted, and filtered through Whatman No. 2 filter paper. Reducing sugars were determined according to the micro method described by Somogyi.[6]

B. 3.2×10^{-2} M, 6.4×10^{-2} M, or 13.9×10^{-2} M sucrose, and 5×10^{-3} M sodium acetate buffer at pH 4.4 or 5.3 (final concentrations), and 1 or 5 ml enzyme solution (1 ml = 2.4–2.5 mg N) in a total volume of 100 ml. 10 or 15 ml samples were withdrawn at zero time and at 22, 44, and 66 h, and the enzyme activity was stopped by adding the sample to an equal volume of 1 N sodium carbonate. The enzyme activity was determined as in A and by polarimetric measurements of the sucrose concentration. The reaction mixture B was used also for determinations of assumed "invertase" activity in the UDPglucose-fructose glucosyltransferase ("transferase") isolated from potato tubers and described earlier.[4]

Results and discussion. The results obtained in this investigation are in good agreement with those reported by Schwimmer *et al.*[5] and McCready.[2] Thus no "invertase" activity was observed in freshly harvested control tubers; in tubers stored for a year, which had well developed sprouts, there was, however, a marked increase of activity. In tubers irradiated immediately or a few months after harvest and analyzed a short time after the irradiation, no "invertase" activity could be shown. In batches of the same tubers, stored for a year or more after irradiation, an "invertase" activity was observed, which was about 50 % of the activity in the preparations from the corresponding control tubers. Some typical results for King Edward tubers are summarized in Table 1. The results obtained for both varieties used were almost equal, although the activity of the "invertase" was somewhat lower in the Bintje variety.

Table 1. β-Fructofuranosidase activity of potato tubers of the King Edward variety, expressed as % sucrose hydrolyzed. I = tubers irradiated 2 weeks after harvest and stored one year after irradiation; C = control tubers stored one year after harvest. Reaction medium: 6.4×10^{-2} M sucrose and 5×10^{-3} M sodium acetate at pH 4.4, and 1 or 5 ml enzyme in a total volume of 100 ml; P = polarimetric determinations; S = reducing sugars determined according to Ref. 6. Number of enzyme isolations: 8 from each group of tubers.

Tubers	Enzyme ml	mg N/ml enzyme	% sucrose hydrolyzed; mean ± error of mean			
			P		S	
			22 h	66 h	22 h	66 h
I	1	2.50	7.4 ± 0.01	16.6 ± 0.11	6.6 ± 0.07	15.9 ± 0.11
I	5	2.50	20.9 ± 0.06	49.0 ± 0.08	17.7 ± 0.15	47.3 ± 0.17
C	1	2.40	12.3 ± 0.08	31.4 ± 0.10	9.5 ± 0.10	28.9 ± 0.10
C	5	2.40	46.3 ± 0.07	100.0 ± 0.00	43.3 ± 0.31	97.3 ± 0.32

The values obtained with polarimetric determinations are considered to be more accurate than those calculated from the amounts of reducing sugars formed. For the micro sugar determinations, the solutions must be highly diluted and the accuracy of the determinations might be impaired by this procedure.

Varying amounts of enzyme solutions were used for the same total volume of reaction mixture in order to investigate whether dilution of the enzyme decreases the effect of the inhibitor of "invertase" as claimed by Schwimmer *et al.*[5] In the present investigation an increase of activity by dilution of the enzyme was also observed. The higher amount of enzyme used caused a slower hydrolysis of the sucrose, *cf.* Table 1.

It should, however, be mentioned that some of the isolated enzyme preparations, even from sprouted control tubers, failed to give any "invertase" activity. The reason for this fact could perhaps be that the "invertase" inhibitor, if present, is more or less developed in the tubers. "Invertase" originating from other biological materials is extremely sensitive to inhibitors, *e.g.* metal ions.[7] The extent of inhibition depends on the degree of purity of the enzyme. However, as only a crude enzyme preparation was used in the present investigation, the possibility is not excluded that small variations in the isolation procedure might influence the activity.

No "invertase" activity, determined by method B, could be observed in the "transferase" preparation isolated from potato tubers as reported in Ref. 4.

It is obvious that the activity of "invertase" in non-irradiated tubers increases with prolonged storage, whereas the "transferase" activity decreases. In irradiated tubers, the "invertase" is inhibited, but the activity of "transferase" is increased. It is undoubtedly quite feasible that the sucrose synthesizing enzyme and the competitive sucrose hydrolyzing enzyme are respectively influenced in opposite directions by prolonged storage and by irradiation of the potato tubers.

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Influence of γ-Irradiation on UDPglucose-Fructose Glucosyltransferase in Potato Tubers

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Several authors [1-4] have shown that UDPglucose is involved in the biosynthesis of sucrose in higher plants. It is well known that the sucrose concentration in potato tubers is influenced by several factors, *e.g.* changes of the temperature, humidity, chemical treatments, and ionizing radiation.

Schwimmer and Rorem [5] reported that the potato tuber is a rich source of UDPglucose-fructose glucosyltransferase ("transferase"). These authors found the highest amount of sucrose to be synthesized at pH 8.1. They pointed out, however, that this pH is perhaps not the true optimum pH of "transferase". The accumulation of sucrose was supposed to be maximal at pH 8.1, while the activity of β-fructofuranosidase ("invertase"), catalyzing the hydrolysis of sucrose, sharply decreased at this pH.

In order to investigate if the marked increase of sucrose in potato tubers, caused by ionizing radiation,[6-9] could be related to changed activity of "transferase", this enzyme was isolated from γ-irradiated, and corresponding non-irradiated, tubers. The activities of the isolated enzyme preparations were determined.