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ACID CATALYSIS IN SOLUTIONS IN THE PRESENCE OF OXIDIZED CARBON

(Presented by Academician A. N. Frumkin on 28 XI 1963)

Previous studies in our laboratory showed (^1) that oxidized carbon, the preparation conditions and properties of which were first described in detail by M. M. Dubinin and (^2), and independently of him by Croit (^3), is a distinctive polyfunctional cation exchanger: part of its exchange capacity (the basic part) is due to ordinary weakly acidic ionogenic groups of the carboxyl and phenolic type, while another part, in accordance with A. N. Frumkin' s concepts (^4, ^5), is due to free hydrogen ions forming the outer sheath of the carbon' s electrical double layer. This gave grounds to assume that oxidized carbon, like synthetic sulfonated cation exchangers (^6-8) and platinized hydrogen carbon (^9, ^10), would serve as an effective catalyst for chemical processes that are accelerated in solutions by hydrogen ions. To verify this assumption we studied a series of catalytic reactions of the acid type in the presence of oxidized carbon. In the present communication, as an example, results are given that were obtained in studying the model reaction of sucrose inversion, previously well studied by other authors both under conditions of homogeneous catalysis by soluble acids (^11) and of heterogeneous catalysis by organic cation-exchange resins (^12, ^13).

The catalyst in our experiments was a macroporous ash-free carbon from a phenol–aldehyde resin, activated in a stream of CO_2 at 900–1000° to a burn-off of ~50%, and then oxidized with atmospheric oxygen at 450°; the ion-exchange properties of the sample prepared in this way fully corresponded to the data of works (^1-4). For comparison, the catalytic action was also studied of the initial nonoxidized carbon, of carbon platinized in a hydrogen atmosphere, of the cation-exchange resins KU-2 and KB-4P-2, and of the homogeneous catalyst —HCl (in the form of 10^{-4}-$10^{-1}N$ solutions). The catalytic experiments were carried out by the usual static method (^6, ^7): to 10 ml of a 5% aqueous sucrose solution a catalyst was added (in most cases in an amount of 0.3 g), and the resulting mixture was heated—with continuous vigorous mechanical stirring —in a flask with a water reflux condenser; the temperature of the thermostat, in which the reaction vessel was placed, 25, 50, or 75°, was maintained constant to within ±0.1°. After a specified time t (0.5–10 hr), the flask was removed from the thermostat, the solution was rapidly cooled to 5–8°, and it was separated

from the catalyst by filtration through an ash-free filter; the invert sugar content in the filtrate was determined by Ofner' s method (^14).

The principal results of our investigations are presented in Tables 1-2 and in Fig. 1. They show first of all (see Table 1) that oxidized carbon is indeed an active catalyst of the sucrose inversion process: although the pH of the solutions after the experiment lay within the limits 5.0-5.5, the catalytic action of the oxidized carbon was approximately equivalent to a $4 \cdot 10^{-3}$ N HCl solution. The effectiveness of oxidized carbon according to Hammett (^15)

was 0.260; for comparison it may be noted that the efficiency of the strongly acidic sulfocationite KU-2, calculated by the same method, proved to be 2.3 times smaller (0.114). With increasing temperature, the rate of inversion, as was to be expected, rose sharply (Fig. 1). At the same time, in experiments with unoxidized carbon, as well as in control experiments—without a catalyst—the percentage of inversion at all temperatures was practically equal to zero.

Table 1

Comparative data on sucrose inversion in the presence of various catalysts ($t = 1$ h; $T = 75°$)

Catalysts	pH of solution after the experiment	% inversion
I. Homogeneous—HCl		
$(C,$ g-eq/l$) \cdot 10^{-4}$	4.2	1.4
Same $\cdot 10^{-3}$	3.1	18.8
Same $\cdot 10^{-2}$	2.0	89.0
II. Heterogeneous		
1. Cation-exchange resins		
a—sulfocationite KU-2	5.0	82.5
b—carboxylic cationite KB-4P-2	4.5	1.9
2. Activated carbons		
a—unoxidized	6.0	0.1
b—oxidized	4.9	48.7
c—hydrogen, platinized	4.7	74.0

As can be seen from the data in Table 2, the kinetics of sucrose inversion by oxidized carbon are well described by the equation for a first-order reaction; moreover, as in the case of catalysis by cation-exchange resins ([12,15]), the rate

constant varied in direct proportion to the carbon charge. The activation energy of sucrose inversion, calculated in the usual way ([12,15]) from the results of the kinetic experiments, proved to be 23.8 kcal/mole,

Table 2

Kinetics of sucrose inversion by oxidized carbon at 50°C

t, h	pH of solution after the experiment	Amount of invert sugar in 10 ml of solution, mg: calculated for 100% inversion	Amount of invert sugar in 10 ml of solution, mg: found after the experiment	% inversion	$k \cdot 10^{-4}$, min^{-1}
1	5.5	526.0	22.1	4.2	7.16
3	5.3	526.0	65.2	12.4	7.35
5	5.8	526.0	102.0	19.4	7.19
10	5.2	526.0	185.4	35.2	7.24

which agrees well with our corresponding data for the homogeneous catalyst—HCl (23.6 kcal/mole)—and with the data of Bodamer and Kunin ([12]) for the sulfocationite Amberlite IR-120 (24.2 kcal/mole).

It is interesting to compare the results of experiments with oxidized carbon and with the weakly cross-linked (2.5% divinylbenzene) monofunctional carboxylic cationite KB-4P-2 (Table 1). Although the exchange capacity of the KB-4P-2 resin at pH 4.5-5.5 exceeded the capacity of oxidized carbon by a factor of 3-4, its catalytic action was practically zero. It follows directly from this that the high efficiency of oxidized carbon must be due to groups considerably more acidic than carboxyl groups. That acid catalysis in solutions on oxidized carbon proceeds by the same mechanism as in the case of hydrochloric acid and sulfocationites and, in all probability, is effected by H^+ ions of the outer sheath of the carbon double layer ([4,5]), is indicated by the good agreement of the activation energies of sucrose inversion in the presence of the three named catalysts ([7]), and also by the fact that the action of oxidized carbon is quite comparable with that of platinized hydrogen carbon of similar porous structure (Table 1), in which ···

catalytically active, evidently, can only be free hydrogen ions ([9], [10]).

It follows from our experiments, therefore, that the ability of active carbon to accelerate the reaction of sucrose inversion is unambiguously determined by the chemical nature of its surface: whereas oxidized carbon—a cation exchanger —exhibits high catalytic activity, ordinary, unoxidized carbon, possessing the

Fig. 1. Kinetics of sucrose inversion by oxidized carbon at 25° (1), 50° (2), and 75° (3)

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properties of an electrochemical anion exchanger ([4], [5]), has no effect at all on the rate of this process. This conclusion is apparently not of a particular, but of a general character—it was verified and confirmed by one of the authors (Z. D. Skripnik) for a whole series of catalytic reactions of the acid type: hydrolysis of esters, esterification, pinacol rearrangement, and others. In addition to its significance for the theory of electrochemical ion exchange on carbon ([4], [5]) and of heterogeneous acid–base catalysis ([16]), the facts established may also be of substantial practical interest, at least in the following two respects. First, oxidized carbons should apparently find practical application as effective, chemically and thermally very stable catalysts for acid-type processes in liquid and vapor* phases. On the other hand, taking into account the influence of the chemical nature of the surface is necessary in all those cases where carbon is used as an adsorbent (for example, for purification of sugar syrups or recovery of ester vapors), and its catalytic action may lead to a reduction in the yield of the target product or to its contamination with foreign impurities.

Fig. 1. Kinetics of sucrose inversion by oxidized carbon at 25° (1), 50° (2), and 75° (3)

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* According to preliminary data obtained by us, the dependence noted above of the catalytic action of active carbons on the chemical nature of their surface remains—in accordance with the concepts of S. Z. Roginsky ([16])—although in a somewhat less pronounced form—also under conditions of vapor-phase acid heterogeneous catalysis.

Note: Figure translations are in progress. See original paper for figures.