

THE MECHANISM OF SACCHARINIC ACID FORMATION

Sir:

An examination of the action of alkali on α -hydroxy- β -methoxy- β -phenylpropiophenone, $C_6H_5CH(OCH_3)CH(OH)COC_6H_5$, would seem to offer a definite means for testing Nef's final theory of saccharinic acid formation [Nef, *Ann.*, **375**, 3 (1910)]. This substance may be regarded as a monomethyl ether of a diphenyltriose. When boiled with alkali it is converted, through a benzylic acid rearrangement of the diketone first formed, to α,β -diphenyllactic acid. The yield of the latter is good.

A more detailed consideration of this reaction than can be given here, makes it clear that such a result definitely requires the separation of oxygen from carbon to occur at the β -carbon atom, since the elimination of the α -hydroxyl group could not reasonably lead to the product obtained. The initial reaction is considered to be of the type of an "aldol dehydration," and its occurrence seems to require the revision of Nef's interpretation of the mechanism by which sugars form saccharinic acids, and perhaps also of the mechanism he advanced to explain the splitting of sugars by alkali.

A discussion of the first of these points will be submitted in the near future.

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ACTIVATED AND VAN DER WAALS ADSORPTION OF AMMONIA AND OF
CERTAIN OTHER GASES

Sir:

Professor H. S. Taylor has presented [*Chem. Rev.*, **9**, 1 (1931); *THIS JOURNAL*, **53**, 578, 3604 (1931)] evidence for two types of adsorption of hydrogen, carbon monoxide, oxygen, nitrogen, water vapor and sulfur dioxide by solids. Van der Waals adsorption proceeds rapidly at low temperatures with small heat and small energy of activation. Catalytically active gas is adsorbed with much larger heat and activation energy, and the rate of adsorption may be relatively slow.

That an adsorbed gas may be bound in more than one way is well known. Thus water is held as hydronium ion (OH_3^+) in perchloric acid monohydrate, as H_2O molecules in gypsum, as hydroxide ion in diaspore ($AlOOH$) and in $Mg(OH)_2$, and as very loosely held H_2O in zeolites [van Arkel and Fritzius, *Rec. Trav. Chim.*, **50**, 1035 (1921)]. Infra-red absorption spectra show indications of two types of binding occurring in certain cases.

The comprehensive investigations of Professor Wilhelm Biltz on adsorption of ammonia vapor by solid halides have furnished several examples of two-type adsorptions. Thus [*Z. anorg. Chem.*, **119**, 115 (1921)] when, at 215° , a little ammonia gas is added to a solid having the composition $\text{MgI}_2 \cdot 4\text{NH}_3$ about one hour is needed to reach pressure equilibrium. Successive small additions of ammonia require longer times until at $\text{MgI}_2 \cdot 5.53\text{NH}_3$ about six hours are required. Over this composition range the equilibrium pressure has risen from 150 to 210 mm. With solids richer in ammonia equilibrium is rapidly established (thirty minutes) but the pressure rises to 595 mm. for the solid $\text{MgI}_2 \cdot 5.84\text{NH}_3$. Biltz explains the first slow reaction in terms of diffusion, and the second rapid reaction as "zeolitic binding" [*cf. Rinne, Neues Jahrb. d. Min.*, II, 28 (1897)] in which the gas molecules enter the crystal lattice without forming good attachment to the other lattice elements. The heat effects are much smaller in this case.

The lead halides [*Z. anorg. Chem.*, **124**, 230 (1922)] show similar effects with ammonia. At -21° about 500 minutes are needed to establish equilibrium. This is followed by rapid adsorption (twenty minutes) accompanied by a pressure increase. Cases of delayed dissociation are also evident [*cf. also Ephraim, Z. physik. Chem.*, **83**, 196 (1913)].

Adsorption of NH_3 on AuCl [*Z. anorg. Chem.*, **148**, 192 (1925)] proceeds in a few minutes at -78° , but at 80 and 99.5° days are required. Delayed equilibria involving the appearance or non-appearance of $\text{AuCl} \cdot 4\text{NH}_3$ are also observed.

Uranium forms two oxides, UO_2 and U_3O_8 , which give definite x-ray patterns [*Z. anorg. Chem.*, **163**, 257 (1927)]. UO_3 is apparently a solid solution of oxygen in U_3O_8 . Starting with $\text{UO}_{3.04}$ at 580° , dissociation to $\text{UO}_{2.91}$ occurs in fifteen minutes but further dissociation to $\text{UO}_{2.84}$ requires 123 hours.

The classic case of hysteresis in gas absorption and evolution is calcite [Le Chatelier, *Compt. rend.*, **102**, 1243 (1886)]. Probably very large activation energies are involved.

At room temperature potassium chlorate is thermodynamically unstable. If equilibrium were rapidly established an oxygen pressure of about 10^{15} atm. would develop.

These cases support the thesis of Professor H. S. Taylor that activated adsorptions and desorptions are fairly general. Catalytic "promoters" may prove to be very useful in providing a mechanism of low activation energy steps and thus eliminating such hysteresis effects.

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