

Complete caproic acid exhaustion.	
	Min. perc. in olfacties.
Amylacetate	1.6
Nitrobenzol	1.3
Terpineol	3.3
Art. Moschus	5.1
Allylalcohol	5.5
Guajacol	5.3
Caproic acid	∞
Pyridin	1.5
Scatol	4.5

GENERAL CONCLUSION.

Amylacetate, nitrobenzol and pyridin are odours for which an olfactory organ that has been exhausted by the smell of terpineol, guajacol or caproic acid is blunted only very slightly. The liminal value is about $1\frac{1}{2}$ times higher than is normally the case. So the anosmia evolved is about $\frac{2}{3}$.

For other qualities of the series of 9 standard-odours (except that for which complete exhaustion exists) the organ is blunted to $\frac{1}{2}$ or $\frac{1}{11}$.

Chemistry. — “*On the Acceleration of Solubility of Metals in Acids by Reducible Compounds.*” By H. J. PRINS. (Communicated by Prof. J. BÖESEKEN.)

(Communicated at the meeting of March 26, 1921).

It is a well-known fact that though there are a great many means available for the reduction of organic compounds, the choice of the reducer greatly contributes to the success of the reduction, so that it is not sufficient to bring hydrogen in status nascens in the presence of the substance that is to be reduced. It ensues from this that there must be a relation between the reducer and the compound that is to be reduced; if this relation were known it would be possible to make a choice with certainty from the available reducers for a definite purpose, or to find new reducers.

Some years ago it was pointed out¹⁾ that in case of reductions the velocity of solubility of the metal in the acid is enhanced by the reducible substance, and that evidently a cooperation, a coaction must take place between metal, acid, and reducible compound in order to bring about the reduction; which is then accompanied by a more rapid dissolving of the metal.

Definite examples of this have not been recorded, except in the literature²⁾ of patents.

Such coactions, which are reckoned among the mutual inductions, are however, known in all kinds of other reactions, especially oxidation reactions. Besides it is known that metals dissolve more rapidly in the presence of oxidizers,³⁾ in such cases it is, however, difficult to decide, whether one has to do with a mutual induction or a subsequent reaction, while the formation of primary oxides assumed by some scientists to take place in such reactions as inter-

¹⁾ PRINS, Chem. Weekbl. 14, 72 (also note) and id. 1004 (1917).

Ibid 11, 476, 477 (1914).

Ibid 12, 38 et seq. (1915).

Journ. f. prakt. Chem. N. F. 89. 448 et seq. (1914).

²⁾ LASSAR COHN, Arbeitsmeth. d. org. Chem.

³⁾ VAN NAME, Chem. Centr.bl. (1914). I 20; (1918). I 257, 907.

SALKOWSKI, Chem. Ztg. 40. 448 (1916).

mediate product, cannot serve as an explanation in the reduction of nitro compounds, aldehydes, and similar substances.¹⁾

Besides for the knowledge of the phenomena of reduction and undoubtedly also for the knowledge of the phenomena of oxidation, more in particular in organic chemistry, this phenomenon of coaction is of importance in that it is in close relation with catalysis, and can easily pass into it.

The possibility that three substances which in couples do not react on each other or in a very small degree, when brought together, react all three on each other follows from the theory of the mutual activation; the catalysis can then be considered as a special case of the coaction, viz. in which two of the three possible reactions between the three components do not take place or only in a very small degree. At the same time this theory explains how such coactions can be realized, and can be changed into a catalytic action in some cases. If two compounds A and B are placed over against a third one, C, and C is built up of two parts in such a way that one part can be attacked by A, the other by B, a coaction may be expected between A, B and C.

It was now the intention to examine a number of systems, consisting of metal, acid or alkali and reducible compound, first of all qualitatively with regard to the influence that the reducible compound has on the velocity of solution of the metal, either with generation of hydrogen or without.

It now appeared that not only nitrobenzene, but also an aldehyde as benzaldehyde exert a surprisingly accelerating influence on the velocity of solution. It is often, especially in the case of nitrobenzene, so great that the metal dissolves from five hundred to a thousand times more rapidly when nitrobenzene is present. Besides it appears, what was also to be expected, that though nitrobenzene has almost always an accelerating action, benzaldehyde is more selective. (See table).

It is further remarkable that the greatest acceleration was observed in those cases in which in the presence of the reducible compound solution of the metal took place, but no generation of hydrogen, which is probably related to the fact that the contact between metal and reducible compound is prevented by the forming hydrogen, which would also point to the probability that the reduction does

¹⁾ SKRABAL, Die induzierten Reaktionen. Samm. Chem. und chem. techn. Vorträge. XIII. Bnd. 10. Heft. 1908.

No.	Metal	Acid	Decrease blank × 1000	Decrease nitrob. × 1000	Decrease Benzald. × 1000	Original weight in gr.	Time in min.
1	Iron wire (<i>h</i>)	6 %/o alcoh. HCl	280	790	90	1.98	70
2	"	4 " "	140	720	90	1.98	70
3	"	1 " "	140	200	100	1.98	75
4	"	80 " acetic acid	10	780	10	1.97	60
5	"	86 " formic acid	75	135	0	1.68	70
6	Zinc wire (<i>e</i>)	100 " acetic acid	40	120	40	1.86	240
7	"	80 " "	260	470	640	1.12	40
8	"	15 " alcoh. acetic acid	20	920	50	1.12	40
9	Zinc leaf (<i>h</i>)	15 " "	30	490	—	1.39	40
10	Lead leaf (<i>l</i>)	6 " alcoh. HCl	30	50	50	1.52	270
11	"	80 " acetic acid	0 in 40 min.	1800 in 3 min.	50 in 40 min.	1.80	—
12	"	70 " acetic acid in acetic acid anhydr.	0 in 40 min.	1150 in 10 min.	40 in 40 min.	1.15	—
13	"	25 " alcoh. acetic acid	13 in 180 min.	3080 in 4 min.	13 in 180 min.	3.08	—
14	"	86 " formic acid	0	460	0	1.39	40
15	"	43 " "	10	850	10	2.13	120
16	"	30 " oleic acid in turpentine	330	1020	320	1.15	70
17	"	10 " lauric acid in paraffin oil	10	225	0	2.07	120
18	Tin leaf (<i>f</i>)	6 " alcoh. HCl	50 in 50 min.	1070 in 10 min.	170 in 50 min.	1.07	—
19	"	80 " acetic acid	10 in 20 min.	690 in 3 min.	6 in 20 min.	0.69	—
20	"	86 " formic acid	0 in 20 min.	470 in 10 min.	0 in 20 min.	0.47	—
21	"	4 " sol. potassium in 90 %/o alcohol	230	560	—	0.67	2 days.
22	Copper gauze (<i>h</i>)	6 " alcoh. HCl	50	1910	—	3.04	200
23	"	6 " alcoh. KCN	250	1330	480	2.57	270
24	Nickel wool (<i>h</i>)	6 " alcoh. HCl	11	144	—	0.441	300
25	Aluminium (<i>h</i>) leaf	1 " alcoh. HCl	50	125	110	0.985	15
26	id. shiny amalg.	4 " alcoh. acetic acid	50	1450	—	1.45	20
27	Silver wire (<i>s</i>)	6 " alcoh. NaCN	4	132	—	0.152	120

(*e*) = electric conduction, is nearly pure.

(*h*) = commercial quality.

(*l*) = so-called tea lead.

(*f*) = tin foil contains a trace of lead.

(*s*) = pure.

To 50 cc. of acid was added 10 cc. of nitrobenzene, resp. benzaldehyde.

not take place through hydrogen in status nascens, but that a coaction between the three components is required.

These preliminary experiments were so executed that only characteristic differences could be expressed; this was desirable in view of the fact that through impurities, presence of different modifications, structure in connection with the treatment, change of the surface in consequence of the solution etc. the metals in themselves can already give differences in the velocity of solution, which might vitiate the conclusions to be drawn.

Use was made of metal in the form of gauze, leaf, or wire, of which a roll or spiral was made, so that the surface that was in contact with the liquid was as much as possible the same. Three rolls of the same weight and surface were now placed in three Erlenmeyer flasks, to each of which the acid was added, and after they had assumed the temperature of the waterbath benzaldehyde was added to the one, nitrobenzene to the second, the third containing only an acid by the side of the metal. As soon as a perceptible action had been exerted on one of the three, or as soon as in one of them the metal was quite dissolved, the metal was taken out of them, washed with water, alcohol, and ether, dried and weighed.

The original weight of the metal, the time, and the decrease are recorded in the following table for a number of the principal experiments.

Unless expressly stated 10 c.c. of nitrobenzene or benzaldehyde was added to 50 c.c. of acid (Cf. the table on the next page).

It appears very clearly from the table that the influence of reducible compounds on the velocity of solution of a metal can be very great, in some cases even so great that most probably there is no longer question of an acceleration of an existing reaction, but of a new one.

Though in almost all cases nitrobenzene shows a very great acceleration, also a compound as benzaldehyde appears to be able to exert a strong positive influence (see N^o. 7, 11, 12, 18, 23, 25).

It is clear that guided by the theory of these reactions shortly mentioned in the beginning, the number of combinations can be extended, which renders it possible greatly to increase the number of reducers, and to define the conditions which a reducer has to satisfy in a definite case.

Thus metal, a salt of hydrochloric acid, a feeble acid (acetic acid), and nitrobenzene may be taken instead of metal, hydrochloric acid, and nitrobenzene, in this way a coaction is realized in a system of four components.

When nitrobenzene is present in great concentration no hydrogen generation is observed; the solution of the metal and the generation of hydrogen is, however, accelerated by a smaller concentration of the nitrobenzene.

Two strips of zinc-leaf, weighing 10.18 gr., surface 38.6 cm², etched with 2 norm. HCl, were placed in 190 cc. of 80% acetic acid, while to one besides 2 cc. of nitrobenzene was added. After having been kept at 73° for 40 min., the zinc was weighed and the generated hydrogen measured. The zinc in the nitrobenzene experiment weighed 7.45 gr., the quantity of hydrogen was 17 cc. (11° and 772 mm.). The zinc in the blank experiment weighed 10.15 gr. and the quantity of hydrogen was 6 cc.

In this experiment there is, however, an unfairness towards the zinc in the blank experiment, because though the two experiments start with the same surface, the nitrobenzene very soon considerably enlarges the surfaces through its strongly corrosive action, which gives it a permanent advantage. Therefore an experiment was made in which the zinc was etched first with diluted hydrochloric acid, then one of the strips of zinc besides with nitrobenzene in 80% acetic acid, and after purification this latter was used for the blank experiment. The result was now as follows:

Weight of the zinc 16.32 gr. Surface 59.2 cm². The conc. of the nitrobenzene was taken still smaller, viz. 2.4 gr. to 170 cc. of 80% acetic acid. A third experiment was made with benzophenone, viz. 3.6 gr. to 170 cc. of 80% acetic acid. In connection with the benzophenone experiment the temperature was chosen 20° higher, i.e. 93°.

After 30 min. the condition was as follows: Weight zinc in blank experiment 16.04 gr., generated hydrogen 50 cc. (temp. 11°, barometer 767 mm.). Weight zinc nitrobenzene experiment: 12.50 gr., generated hydrogen 115 cc. Weight zinc benzophenone experiment: 16.09 gr., generated hydrogen 10 cc.

It appears from this, just as from the table that a reducible compound can exert both an accelerating and a retarding influence as well on the dissolving of the metal and on the hydrogen generation.

Finally a similar experiment was made with zinc that had been etched in boiling 30% acetic acid, to which nitrobenzene was added, so that the nature of the zinc surface was the same as in the presence of nitrobenzene for all experiments. The quantity of benzophenone was doubled, so that the quantity of reducible oxygen was equal to that of nitrobenzene.

Weight zinc: 14.32 gr., surface 60 cm². Blank experiment contained 170 cc. of 80% acetic acid; the two others resp. 2.4 gr.

of nitrobenzene and 7,2 gr. of benzophenone. The temperature was kept at 65—66°.

After an hour the condition was as follows:

Weight zinc blank experiment: 14,08 gr. Generated hydrogen: 45 cc. (temp. 14°. Barometer 770 mm.).

Weight zinc nitrobenzene experiment: 10,47 gr., generated hydrogen: 142 cc.

Weight zinc benzophenone experiment: 14,19 gr., generated hydrogen 8 cc.

Here too benzophenone gives a retardation, it appearing at the same time from the comparison with the hydrogen generated in the blank experiment that part of the hydrogen has been used for the reduction of the benzophenone. It seems, therefore, that the nature of the surface has no influence on the qualitative result

According to the way indicated above it is further possible to take in these experiments more intricate systems, in which through coaction reactions are brought about or accelerated. Thus in the mixture of metal, hydrochloric acid, and nitrobenzene, the hydrochloric acid can be replaced by a feeble acid, as acetic acid, and a salt of hydrochloric acid.

Then a coaction takes place between four compounds:

1. Copper with 50 cc. 80% acetic acid and 5 gr. CaCl_2 .
Decrease 0.180 gr.
2. Copper with as above, and 5 cc. nitrobenzene. Decrease 0.065 gr.
3. Copper with 50 cc. 70% alcohol and 5 gr. CaCl_2 . Decrease 0.015 gr.
4. Copper with alcoh. as above and CaCl_2 as above, and 5 cc. nitrobenzene. Decrease 0.005 gr.
5. Copper with 50 cc. 80% acetic acid and 5 gr. CaCl_2 and 5 cc. nitrobenzene Decrease 0.245 gr.

Similar coactions, the explanation of which rests likewise on the considerations given above are met with in the oxidation of organic compounds, and can be most clearly shown by the study of the velocity of dissolving of metal-peroxides in acids whether in presence of oxidizable compounds or not. Experiments on this subject are still in progress.

It appears from the above preliminary experiments that there is a cooperation, a coaction between metal, acid and reducible compound, which is to be explained by this that a certain mutual activation of the components must take place if the reduction is to appear in a considerable degree. This appears to be the case both in alcoholic and aqueous acetic acid solution, and in anhydrous acetic or paraffin.