Chemistry. — "*Heterogeneous catalysis and the orientation of adsorbed molecules*". By Prof. H. R. KRUYT and C. F. VAN DUIN.

(Communicated at the meeting of September 30, 1922).

In a previous communication[1]) we published investigations on the relation between the adsorbtion of reacting substances an the velocity of the reaction, with the object of coming to a better understanding of heterogeneous catalysis. In these investigations we found, that by giving coal to the reacting system a decrease of the velocity sets in, even in cases, where undoubtedly an increase of the reacting components in the surface layer takes place.

In accordance with the theory of I. LANGMUIR[2]) and W. D. HARKINS[2]) concerning the special condition of molecules, which are situated in surface layers, we tried to explain our results by the assumption 1. that adsorbed molecules have partly lost their mobility and consequently a great deal of the possibility of meeting and reacting with other molecules, and 2. that adsorbtion can cause positive catalysis only in the case, when the molecules are adsorbed in such a way that the number of effective collisions increases.

That adsorbtion in itself can have a decreasing effect was found when studying a monomolecular reaction, viz. the transformation of racemic dibromo-succinnic acid into bromo fumaric acid and HBr[4]). The results are given in the tables I and II.

Evidently a marked decrease in the velocity occurs.

We discussed in the paper cited above, that a positive contact catalysis can be expected only in the case, when the reacting group is turned away from the adsorbent and towards the surrounding liquid. With charcoal as an adsorbent, and water as milieu, all electrically polar groups will be turned towards the water; we therefore had chosen the reaction of $\alpha\beta$ dibromo-propionic acid and KJ (formation of acrylic acid, KBr and J_2). As might have been

[1]) Rec. trav. chim. Pays Bas **40**, 249 (1921).

[2]) Journ. amer. chem Soc. **39**, 354 en 541 (1917).

[3]) Journ. amer. chem. Soc. **38**, 2221 (1916) and **39**, 1848 (1917).

[4]) Cf. HOLMBERG, Journ. f. prakt. Chem. **84**, 145 (1911) and Zeitschr. f. physik. Chem. **79**, 147 (1912).
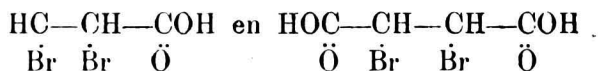
TABLE I. *Without* coal.

Time in min.	c.c. NaOH $^1/_{20}$ n p. 10 cc.	conc. in $\frac{n}{400}$	k mono-mol.
0	20.22	19.98	—
1371	21.53	17.36	0.000103
2991	22.70	15.02	095
4288	23.57	13.28	095
6771	24.88	10.66	093

TABLE II. *With* coal.

Time in min.	c.c. NaOH $^1/_{20}$ n p. 10 cc. not corr.	c.c. NaOH $^1/_{20}$ n p. 10 cc. corr.	conc. in $\frac{n}{400}$	k mono-mol.
0	18.91	20.22	19.98	—
1372	19.89	21.20	18.02	0.000075
2992	20.87	22.18	16.06	73
4311	21.29	22.60	15.22	63
6788	22.12	23.43	13.56	57

expected, we then have found and accelleration of the reaction. We repeated these experiments in a CO_2-atmosphere and in the dark room to avoid complications. The result was almost the same: without coal we found k = 0.000123 and when coal was added k = 0.000149.

The place of the polar groups in dibromo-propionic acid is however not symmetric; the possibility remains that the COOH-group exerts a more vigorous orientating influence than the Br groups and consequently the latter will not be in a most favourable condition. A better result could be expected therefore in the case of the reaction of dibromo-succinic acid and KJ. A comparison between the formulae

$$\begin{array}{ccc} \text{HC—CH—COH} & \text{en} & \text{HOC—CH—CH—COH} \\ \text{Br} \quad \text{Br} \quad \text{Ö} & & \text{Ö} \quad \text{Br} \quad \text{Br} \quad \text{Ö} \end{array}$$

will elucidate this immediately. Moreover, the stereochemical configuration suggests a still better arrangement in the case of the mesoform than in that of the racemic. In the tables III and IV we give the results obtained with the racemic, in the tables V and VI

TABLE III.

R a c e m i c-acid *without* coal.

Time in min.	c.c. thio $\frac{n}{40}$	conc. $^n/800$	k mono-mol.
0	0.08	19.92	—
790	1.82	18.18	0.000116
1392	2.99	17.01	113

k mean 0.000115

TABLE IV.

R a c e m i c-acid *with* coal.

Time in min.	c.c. J $\frac{n}{40}$ not corr.	c.c. J $\frac{n}{40}$ corr.	conc. $^n/800$	k mono-mol.
0	17.27	20.12	19.92	—
776	11.72	14.57	14.37	0.000421
1380	8.90	11.75	11.55	395

k mean 0.000408

21

TABLE V.			
Meso-acid *without* coal.			

Time in min.	c.c. thio $\frac{n}{40}$	conc. $n/800$	k mono-mol.
0	0.06	19.94	—
289	1.11	18.89	0.000187
576	2.12	17.88	189
806	2.83	17.17	186

k mean 0.000187

TABLE VI.				
Meso-acid *with* coal.				

Time in min.	c.c. J $\frac{n}{40}$ not corr.	c.c. J $\frac{n}{40}$ corr.	conc. $n/800$	k mono-mol.
0	18.21	20.14	19.94	—
292	14.45	16.38	16.18	0.000716
582	11.20	13.13	12.93	744
809	9.47	11.40	11.20	713

k mean 0.000724

those with the meso-acid. The initial concentration of the acid was $^1/_{40}$ n., that of KJ 2n.; work is done at 25° centigrade, in CO_2-atmosphere, in the dark room; 1 gramm of coal was added per 100 ccm.; in the experiments with coal 10 ccm. of the reacting mixture were poured into 20 ccm. of thio-solution of 0.02525 n.; the titration was done with a J-solution of $^1/_{40}$ n.

These results, shewing a great accelleration of the reactions, fully support our theory.

We have still other expirience, which is in accordance with this theory. Dr. C. F. VAN DUIN wil give presently a detailed paper in Recueil des Travaux chimiques des Pays Bas.

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