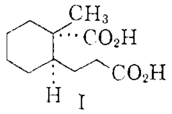
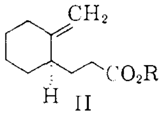
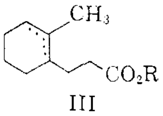
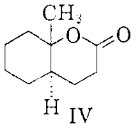
The synthesis of carboxylic acids has been carried out industrially in the presence of water or proton acids. We wish to point out that the reaction is general to any system which contains a carbonium ion. Thus silver fluoroborate or silver perchlorate in nitrobenzene solution with a tertiary halide constitute such a system which in the case of *t*-amyl chloride gave a quantitative yield of tertiary carboxylic acid. With the stable tropylium ion[8] a *ca.* 10% conversion into acyl bromide was obtained even at an atmospheric pressure of carbon monoxide.

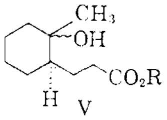
Further studies will be needed to determine the limitations and stereospecificity of this reaction in more complex systems.


I


II


III


IV


V

---

[8] W. von E. Doering and L. H. Knox, THIS JOURNAL, **79**, 354 (1957).

CHANDLER LABORATORY
COLUMBIA UNIVERSITY GILBERT STORK
NEW YORK 27, N. Y. MALCOLM BERSOHN

RECEIVED JANUARY 14, 1960

LOCATION OF HYDROXYLS ON SILICA-ALUMINA CATALYSTS

Sir:

It has been called to our attention[1] that the equation for calculating the per cent. of hydroxyls on aluminum in silica-alumina from the Boron Number should be $f(\text{Al}) = \text{B}_n/(3 - 2\text{B}_n)$ rather than[2] $f(\text{Al}) = \text{B}_n/(1.5 - 0.5\text{B}_n)$. Consequently Table II of our publication[2] should be corrected:

Temp. of activation, °C.	Boron number	% of total hydroxyls on aluminum
250	0.21	8
325	.29	12
	.42	19
400	.48	24
	.53	27
500 (20 hr.)	.30	13
	.41	19

This change in values of the per cent. of total hydroxyls on aluminum fortunately does not affect the discussion concerning the location of hydroxyls in silica–alumina.

It also was pointed out[1] that the per cent. hydroxyls on alumina calculated on the basis of measured H_2/B_2H_6 ratios (1.9 at 250°, 1.3 at 400°) differ from those calculated from the corresponding boron numbers. This difference is only apparent and arises when the calculations are based upon the assumption that the reaction of diborane with silica in silica–alumina results in a constant hydrogen to diborane ratio of approximately three for the silica component. However, this ratio may vary with temperature. To demonstrate this effect we have calculated the per cent. hydroxyl on alumina based on the boron number and based on the experimentally obtained $H_2:B_2H_6$ ratios as a function of the $H_2:B_2H_6$ ratio on the silica component. These data are presented in the table.

Temp. of activation	Assumed H_2/B_2H_6 ratio for OH's on Si	Calculated % OH on alumina From boron no.	Calculated % OH on alumina From H_2/B_2H_6
250	3.0	8.1	29
	2.5	9.6	21
	2.2	10.8	13
	2.1	11.3	9.6
	2.0	11.7	5.3
400	3.0	24	65
	2.5	27	62
	2.0	32	54
	1.7	35	44
	1.6	37	38
	1.5	38	31

From interpolation the calculated percentages by the two methods are equal at a ratio of 2.14 at 250° and at a ratio of 1.58 at 400°. The corresponding values for the per cent. of hydroxyls on aluminum are 11 and 37, respectively. These values are probably more accurate than those based upon a hydrogen to diborane ratio of three for the silica component such as used in calculating the values in Table II.[2] The boron number, by virtue of its independence of the hydrogen to diborane ratio of silica, appears to be the better criterion for comparing a number of different silica–alumina samples.

NATIONAL ENGINEERING SCIENCE CO. H. G. WEISS
PASADENA, CALIFORNIA J. A. KNIGHT
HUGHES TOOL CO., AIRCRAFT DIVISION
CULVER CITY, CALIFORNIA I. SHAPIRO

RECEIVED DECEMBER 28, 1959

---

[1] P. Zwietering, Staatsmijen im Limburg, Centraal Laboratorium Geleen (Netherlands), private communication.

[2] H. G. Weiss, J. A. Knight and I. Shapiro, THIS JOURNAL, **81**, 1823 (1959).

A STUDY OF THE INTERACTION BETWEEN CARBON AND DISSOCIATED GASES

Sir:

Active nitrogen[1] generated by passing nitrogen through an electrodeless discharge, was pumped over a spectroscopic carbon rod at 800°. The reaction products condensable at liquid nitrogen temperature were collected and analyzed by infrared spectroscopy. No cyanogen was ever obtained, indicating that the macroscopic reaction between carbon and active nitrogen is extremely inefficient.

However, when nitrogen containing about 30 p.p.m. of added hydrogen was activated and passed over the carbon rod, considerable HCN was obtained. About 20% of the added hydrogen was recovered as HCN and 50% was recovered as NH_3. The average rate of HCN production was independent of the total time that the carbon was exposed to active nitrogen. Control experiments showed that the presence of both the carbon rod and the hydrogen was necessary to obtain significant amounts of HCN. By means of titration

---

[1] K. R. Jennings and J. W. Linnett, *Quart. Rev.*, **12**, 116 (1958).