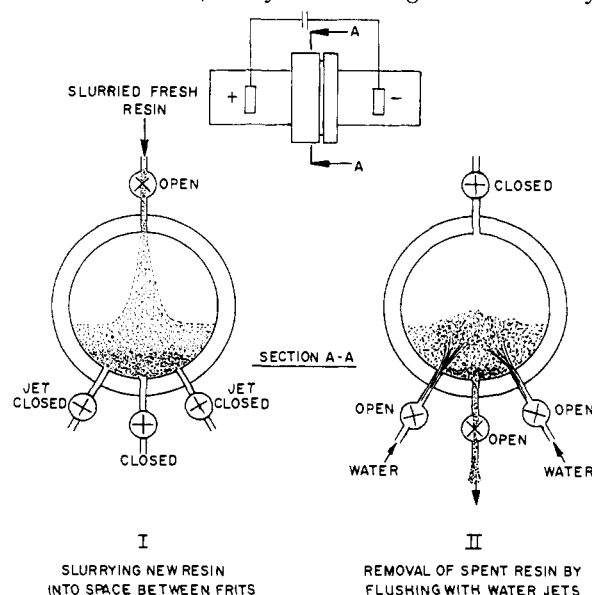


TABLE I
NITRATE ION TRANSFER ACROSS INORGANIC
ANIONIC MEMBRANE AT 25°

Start- ing concn. HNO ₃ , N	Aver- age cur- rent, amp.	Cur- rent den- sity (amp. ft. ⁻²)	Time, hr.	Amp., hr.	Equivalents		% Ef- ficiency
					Actual	Theo- retical	
a Present in both anode and cathode compartments.							
0.3	0.351	28.7	0.99	0.344	0.00708	0.0128	55.4
.3	.335	27.3	1.02	.340	.00985	.0127	77.6
.3	.275	22.3	0.55	.151	.00345	.33564	62.8
.1	.119	9.70	1.00	.119	.00445	.00313	70.5
.1	.197	16.1	1.80	.355	.0065	.00527	81.0
.1	.096	7.85	1.00	.096	.00358	.00301	84.0

made by slurring finely divided ion exchange resins between two fine frits which act as supporting walls, as shown in Fig. 1. Replacement of the spent membranes involved merely flushing the ion exchange resin out from between the frits by means of water jets and allowing a slurry of new resin to settle in its place. The entire replacement is made by a simple remote manipulation of valves.

Since the denitration of radioactive waste resulting from fuel element dissolution is a potential use for permselective membranes (anionic), efficiencies were determined by the transfer of the nitrate ion. First frits 1.5" in diameter with no ion exchange material between them were used to separate the two compartments of an electrolytic cell, and the resulting efficiency was found to be 16%. This value is in agreement with the theoretical value based on the relative velocities of the nitrate and hydrogen ions with the frit acting merely as a diffusion barrier. With ion exchange resin between the frits, the efficiencies were much higher (Table I), which showed that this type of membrane does have permselectivity to an extent that might be practically useful. To determine extent of upstream diffusion, 5.8×10^6 disintegrations per minute per milliliter of cesium-137 was placed in the cathode compartment of the cell. None of this isotope could be detected in the anode compartment after several hours of operation. If the radiation is moderate, finely divided organic resins may



be expected to give extended service. In higher radiation fields a slurry of organic resin will require frequent changing and inorganic ion exchangers of sufficient chemical stability are preferable.

To date membranes made from slurried resins have been studied on a bench scale only so that economic comparison with membranes containing a matrix is not justifiable; however, economy of easy replacement should be considered in the light of any increased installation cost and lower current efficiencies.

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RECEIVED JANUARY 11, 1960

A STEREOSPECIFIC REACTION OF CARBON MONOXIDE

Sir:

We wish to report on the stereochemistry of tertiary acid synthesis *via* high pressure reaction with carbon monoxide, and incidentally on an extremely facile synthesis of *trans*-2-methyl-2-carboxy-1-cyclohexanepropionic acid (I), a substance of considerable interest because of its conversion to *trans*-8-methylhydrindanone-1, the typical C/D ring system of the steroids.^{1,2}

A mixture of ethyl 2-methylenecyclohexanepropionate (II)³ with concentrated sulfuric acid was kept for several days under a carbon monoxide pressure of two hundred atmospheres.⁴ The product from the reaction proved to be the *trans*-dicarboxylic acid I, formed in 80% yield. The melting point (178–179°) was not depressed upon admixture with an authentic sample.²

Similarly, and not unexpectedly, the mixture of olefinic esters (III) and lactone (IV) obtained together in the dehydration of V⁵ also produced a high yield of I under the above conditions.

The ready decarboxylation of tertiary carboxylic acids in concentrated sulfuric acid made it appear very unlikely that the observed stereospecificity could be the result of kinetic control. We have been able to show that the product is indeed determined by thermodynamic considerations⁷ by demonstrating that *cis* 2-methyl-2-carboxy-1-cyclohexanepropionic acid² is transformed into the *trans* isomer (I) under the conditions which led to its formation from II, III and IV. These results imply further that the steric requirements of the carboxyl group (quite possibly as its anhydride with sulfuric acid) are greater than that of a methyl group, perhaps because of the solvation requirements of the protonated function.

(1) W. E. Bachmann and S. Kushner, *THIS JOURNAL*, **65**, 1963 (1943).

(2) W. S. Johnson, *ibid.*, **66**, 215 (1944).

(3) This substance was prepared in this Laboratory by Dr. S. D. Darling from ketene and ethyl 2-oxocyclohexanepropionate⁶ by a procedure which will be reported separately.

(4) Synthesis of tertiary acids, using the system olefin or alcohol, strong acid and carbon monoxide has been effected frequently, e.g., T. A. Ford, H. W. Jacobson and T. C. McGrew, *THIS JOURNAL*, **70**, 3793 (1948), and H. Koch, *Brennstoff-Chem.*, **36**, 321 (1955).

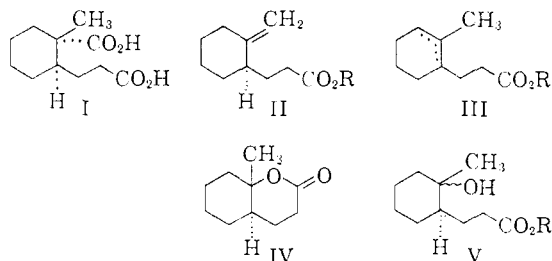
(5) From the reaction of ethyl 2-oxocyclohexanepropionate⁶ with methylmagnesium iodide.

(6) G. Stork and H. K. Landesman, *THIS JOURNAL*, **78**, 5128 (1956).

(7) Another case of equilibrium control in a related reaction has been reported very recently by R. E. Pincode, E. Grigat and P. D. Bartlett, *ibid.*, **81**, 6332 (1959).

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 ion⁸ 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.



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

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GILBERT STORK
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RECEIVED JANUARY 14, 1960

LOCATION OF HYDROXYLS ON SILICA-ALUMINA CATALYSTS

Sir:

It has been called to our attention¹ that the equation for calculating the per cent. of hydroxyls on aluminum in silica-alumina from the Boron Number should be $f(\text{Al}) = B_n / (3 - 2B_n)$ rather than² $f(\text{Al}) = B_n / (1.5 - 0.5B_n)$. Consequently Table II of our publication² 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 out¹ that the per cent. hydroxyls on alumina calculated on the basis of measured $\text{H}_2/\text{B}_2\text{H}_6$ 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

(1) P. Zwietering, Staatsmijn in Limburg. Centraal Laboratorium Geleen (Netherlands), private communication.

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

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 $\text{H}_2/\text{B}_2\text{H}_6$ ratios as a function of the $\text{H}_2/\text{B}_2\text{H}_6$ ratio on the silica component. These data are presented in the table.

Temp. of activation	Assumed $\text{H}_2/\text{B}_2\text{H}_6$ ratio for OH's on Si	Calculated % OH on alumina	
		From boron no.	From $\text{H}_2/\text{B}_2\text{H}_6$
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.

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I. SHAPIRO

RECEIVED DECEMBER 28, 1959

A STUDY OF THE INTERACTION BETWEEN CARBON AND DISSOCIATED GASES

Sir:

Active nitrogen¹ 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).