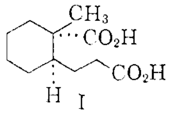
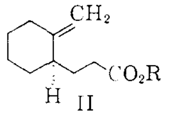
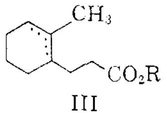
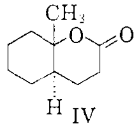
The synthesis of carboxylic acids has been carried out industrially in the presence of water or proton acids. We wish to point out that the reaction is general to any system which contains a carbonium ion. Thus silver fluoroborate or silver perchlorate in nitrobenzene solution with a tertiary halide 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.

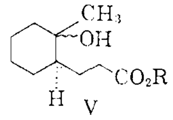
Further studies will be needed to determine the limitations and stereospecificity of this reaction in more complex systems.


I


II


III


IV


V

---

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

CHANDLER LABORATORY
COLUMBIA UNIVERSITY
NEW YORK 27, N. Y.
GILBERT STORK
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 $f(\mathrm{Al}) = \mathrm{B}_n/(3 - 2\mathrm{B}_n)$ rather than[2] $f(\mathrm{Al}) = \mathrm{B}_n/(1.5 - 0.5\mathrm{B}_n)$. 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.	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.
PASADENA, CALIFORNIA
H. G. WEISS
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).

of the active nitrogen with NO,[2] it was found that the atomic nitrogen concentration over the carbon was the same whether pure nitrogen or the nitro-hydrogen mixture was used. Assuming the hydrogen was completely dissociated over the carbon, it was found that the N:H ratio over the carbon was at least 10:1. It is hypothesized that the atomic nitrogen is chemisorbed on the carbon and that this chemisorbed nitrogen perturbs the adjacent carbon–carbon bonds. A hydrogen atom then reacts with the chemisorbed CN forming HCN with a collision efficiency of at least 10^{-3}. It is known that at 600° hydrogen atoms react in an analogous way with cyanogen.[3]

This research was carried out at the General Electric Company Missile and Space Vehicle Department, Aerosciences Laboratories, Philadelphia, Pa., under sponsorship of the Ballistic Missile Division, U. S. Air Force, Contract No. 04(647)-269, and a detailed account of it is to be published elsewhere.[4]

---

(2) P. Harteck, P. R. Reeves and G. Manella, *J. Chem. Phys.*, **29**, 608 (1958).

(3) E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd Edition, Reinhold Publishing Corp., New York, N. Y., 1954, p. 636.

(4) W. G. Zinman, "Proceedings of the Conference on Physical Chemistry in Aerodynamics and Space Flight," 1959, to be published.

REPUBLIC AVIATION CORPORATION
MATERIALS DEVELOPMENT LABORATORY
FARMINGDALE, LONG ISLAND
NEW YORK
WALTER G. ZINMAN

RECEIVED JANUARY 11, 1960

UNIVALENT RUTHENIUM

Sir:

We wish to report a new type of ruthenium complex, in which the central atom displays the unusual oxidation state I. Chloro-tris-(triphenylphosphine)-ruthenium(I) is obtained in 96% yield by treating ruthenium(III) chloride[1] with an excess of triphenylphosphine (P/Ru, 6–12/1) in boiling ethylene glycol monomethyl ether (124°), the tertiary phosphine being the sole reducing agent in the system

$$RuCl_3 + 4Ph_3P \longrightarrow [RuCl(Ph_3P)_3] + Ph_3PCl_2$$

Anal. Calcd. for $RuClP_3C_{54}H_{45}$: Ru, 10.95; Cl, 3.84; P, 10.06; C, 70.24; H, 4.91. Found: Ru, 11.27; Cl, 3.80; P, 9.85; C, 69.09; H, 4.89.

The yellow crystals of the univalent complex are stable in air (m.p. 139°) and essentially diamagnetic (μ_{eff} = 0.28 B.M., 27°). The compound is a non-electrolyte in nitrobenzene (Λ_M = 0.2 for a 6×10^{-4} molar solution); its apparent molecular weight in chloroform, 492, indicates extensive dissociation (formula weight, 923), and is therefore inconclusive with respect to the possible presence of a polynuclear species.

The corresponding triphenylarsine derivative, $RuCl(Ph_3As)_3$, is synthesized in an analogous manner, but the compound results only after prolonged refluxing. (*Anal.* Calcd. for $RuClAs_3C_{54}H_{45}$: Ru, 9.58; Cl, 3.36; As, 21.30; C, 61.46; H, 4.30. Found: Ru, 9.36; Cl, 3.69; As, 20.65; C, 61.03; H, 4.52.) Even more vigorous conditions are required for the preparation of bromo-tris-(triphenylphosphine)-ruthenium(I): the complex is formed from $RuBr_3$ and $(C_6H_5)_3P$ in ethylene glycol at 190°. (*Anal.* Calcd. for $RuBrP_3C_{54}H_{45}$: Ru, 10.45; Br, 8.26; P, 9.60; C, 67.01; H, 4.69. Found: Ru, 10.98; Br, 8.29; P, 9.38; C, 66.78; H, 4.99.)

According to their X-ray powder diffraction patterns the Ru(I) complexes with triphenylphosphine and triphenylarsine are isomorphous with each other, and with the recently discovered osmium complexes of the same type, $[OsX(Ph_3M)_3]$ (X = Cl, Br; M = P, As).[2] The chemical properties of the univalent osmium and ruthenium complexes are also rather similar. Generally, the ruthenium(I) compounds appear to be more reactive with respect to dissociation.

The diamagnetism of $[RuCl(Ph_3P)_3]$ suggests exchange interaction between two neighboring ruthenium(I) atoms of d^7 configuration, and thus a dimeric structure which would provide for a relatively short Ru–Ru distance (*cf.* ref. 2). Regardless of what the actual configuration of the complex may be, it seems likely that ruthenium is effectively quinquecovalent. This is reminiscent of the quinquecovalent iron(I) complex, $[Fe(CO)_2(diarsine)I]$, reported recently by Nigam, Nyholm and Rao,[3] who also point out that there exists a whole series of isoelectronic (d^7) quinquecovalent compounds: Mn(O), Fe(I), Co(II), and Ni(III) (for references, see 3). These complexes are monomeric and *paramagnetic*, however, and therefore not strictly analogous with the present case.

The only solid compound presumed to contain Ru(I), RuX(CO) (X = Br, I),[4,5] that has been reported previously, is most likely a polymer of unknown complexity.[5] Jørgensen[6] summarizes critically the many arguments concerning the existence of ruthenium(I) in aqueous solution (for references, see ref. 6), and concludes that Ru(I) disproportionates in a few minutes to the metal and Ru(II).

Other new complexes of ruthenium with triphenylphosphine and triphenylarsine which have been synthesized in the present study include $[Ru^{II}Cl_2(Ph_3P)_3]$, $[Ru^{III}Cl_3(Ph_3As)_3]$ and $[Ru^{III}X_3(Ph_3M)_2]$ (X = Cl, Br; M = P, As). Details of this and related work will be reported in a later communication.

MELLON INSTITUTE
PITTSBURGH, PA.
L. VASKA
ELEANOR M. SLOANE

RECEIVED JANUARY 13, 1960

---

(1) Commercial "hydrated ruthenium chloride"; analysis in this laboratory gave Ru/Cl = 1/2.84.

(2) L. Vaska, "International Conference on Co-ordination Chemistry," The Chemical Society (Special Publication No. 13), London, 1959, p. 145; *Z. Naturforschg.*, **14b**, in press (1959).

(3) H. Nigam, R. S. Nyholm and D. V. Ramana Rao, *J. Chem. Soc.*, 1397 (1959).

(4) W. Manchot and E. Enk, *Ber.*, **63B**, 1635 (1930).

(5) R. S. Nyholm, Report to the 10th Solvay Council, Brussels, 1956, p. 272.

(6) C. K. Jørgensen, *Acta Chem. Scand.*, **10**, 518 (1956).