and at 1 atm. and 25° it follows that $K_{\mathrm{FeCl^{+2}}}$ is 21 M^{-1}. This value is in agreement with Bray and Hershey[8] and Badoz-Lambling[9] but is higher than the values reported by other investigators. Similar analysis for the $Fe(NO_3)_3$–HNO_3 solutions using a value of 50 for $\Lambda^0_{\mathrm{FeNO_3^{+2}}}$ yields a $K_{\mathrm{FeNO_3^{+2}}}$ of 5.7 M^{-1}, which is in reasonable agreement with the results of Sykes[10] but again higher than the value reported by some other investigators. Repeating these calculations at the higher pressures we find that the formation constant of $FeCl^{+2}$ decreases 20-fold from 21 to 0.4 M^{-1} in going from 15 to 30,000 p.s.i., whereas the formation constant of $FeNO_3^{+2}$ decreases only from 5.7 to 4.6 M^{-1} in going from 15 to 70,000 p.s.i.

One might expect that the effect of pressure on ion-pair formation should be less than upon true complex ion formation inasmuch as the former requires fewer alterations in solvation and, hence, does not entail large volume changes. Such being the case, the present results suggest that $FeCl^{+2}$ is a complex ion, but that $FeNO_3^{+2}$ is an ion pair, that is to say, the composition of the innermost hydration spheres of the participants is unchanged.

Acknowledgments.—We wish to acknowledge the valuable assistance of Professor R. M. Fuoss of Yale University and Dr. M. L. Vidale.

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Hydrolysis of Neutron-Irradiated Uranium Monocarbide[1]

BY M. J. BRADLEY, J. H. GOODE, L. M. FERRIS,
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The reaction of neutron-irradiated uranium monocarbide with water at 80° is markedly different from that of unirradiated uranium monocarbide.[2] After irradiation to 6000 and 16,000 Mwatt-days/metric ton of total uranium (0.6 and 1.6 atom % burnup), uranium monocarbide specimens were nearly inert to water at 80 and 100°. In contrast, 4-g. specimens of unirradiated monocarbide reacted completely with 80° water within 3 hr. Hydrolysis of specimens that had been irradiated to the relatively low level of 600 Mwatt-days/metric ton of total uranium (0.06 atom % U burnup) yielded 96 ml. (STP) of gas per g. of carbide, consisting of 67 volume % methane, 28% hydrogen, and small quantities of higher hydrocarbons (Table I). In contrast, the gaseous products from the hydrolysis of unirradiated specimens from the same batch of carbide as the irradiated specimens contained much more methane (88 volume %) and less hydrogen (9%).[3] Only 86% of the original carbide carbon was found in the gaseous products from the slightly irradiated specimen, *vs.* essentially all of the carbon from the unirradiated specimens. In both cases the nonvolatile hydrolysis residue dissolved completely in 6 *N* HCl yielding a solution of tetravalent uranium (and fission products, if irradiated). Heating unirradiated specimens in a niobium capsule for 3 weeks (the length of the irradiation period) at 800° (the approximate temperature of the carbide during irradiation) had no effect on the hydrolysis behavior, indicating that the effect observed with the irradiated specimens was not thermally induced.

TABLE I

EFFECT OF NEUTRON-IRRADIATION LEVEL ON THE HYDROLYSIS OF URANIUM MONOCARBIDE AT 80°

Specimen burnup, Mwatt-days/metric ton of uranium	0	0[a]	600	6000	16,000
Vol. of gas evolved, ml./g. at STP	90.4	89.7	96.2	No reaction in 24-hr. tests	
Gaseous products, vol. %					
Hydrogen	8.9	8.5	28		
Methane	88	88	67		
Ethane	1.88	2.33	3.01		
Propane	0.44	0.43	0.52		
Butane	0.23	0.20	0.34		
C_5–C_8 alkanes	0.09	...	0.10		
Alkenes	0.20	0.08	0.48		
Alkynes	...	0.01	0.08		
Unidentified	0.01	0.09	0.26		
Carbon in gas, % of total	98	97	86		
Reaction time, hr.	3	3	>6		

[a] Specimen heated for 3 weeks at 800° in a niobium capsule.

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(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) M. J. Bradley and L. M. Ferris, *Inorg. Chem.*, **1**, 683 (1962).

(3) M. J. Bradley, L. M. Ferris, T. Hikido, and J. W. Ullmann, U. S. Atomic Energy Commission Report ORNL-3403 (March 19, 1963).

CONTRIBUTION FROM THE MCPHERSON CHEMISTRY
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The Compounds $(B_5H_8)_2CH_2$ and $B_5H_8CH_2BCl_2$

BY E. R. ALTWICKER, G. E. RYSCHKEWITSCH,[1]
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In a recent paper[2] we presented evidence that alkylation of pentaborane-9, B_5H_9, with olefins and alkyl halides in the presence of aluminum chloride is a general reaction of B_5H_9 and leads to substitution on the apex

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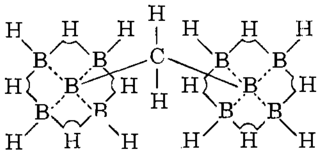
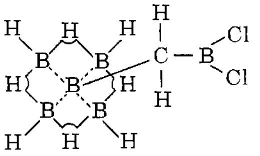
(2) G. E. Ryschkewitsch, S. W. Harris, E. J. Mezey, H. H. Sisler, E. W. Weilmuenster, and A. B. Garrett, *Inorg. Chem.*, **2**, 890 (1963).

boron atom. We are now able to report that in the course of experiments with halomethanes we were able to isolate, among others, two new derivatives of B_5H_9, di(1-pentaboryl)methane, $(B_5H_8)_2CH_2$ (I), and (1-pentaboryl)dichloroborylmethane, $(B_5H_8)CH_2BCl_2$ (II).[3]


I


II

Reactions with methylene chloride, methylene bromide, and chlorobromomethane lead to rather similar results. In a typical reaction B_5H_9 (64.4 mmoles), CH_2Cl_2 (26.5 mmoles), and $AlCl_3$ (4.3 mmoles) were heated together in a sealed 500-ml. Pyrex flask at 70° for 5 hr. To guard against the consequences of possible explosions the flask was enclosed by a wire mesh protection. On vacuum fractionation 40% of the original B_5H_9 was recovered. The highly volatile portion of the reaction products consisted of H_2 (13.6 mmoles), HCl (1.1 mmoles), B_2H_6 (0.3 mmole), and a trace of BCl_3. A crystalline material and a liquid, which proved to be $(B_5H_8)_2CH_2$ (1.2 mmoles) and $B_5H_8CH_2BCl_2$ (0.3 mmole), respectively, were trapped at $-36°$. A considerable amount of low-volatile material remained and was not further analyzed.

Separation of the mixture, although difficult, was accomplished by a careful distillation from a simple microstill into a small fractionation train, followed by sublimation of the crystalline $(B_5H_8)_2CH_2$ fraction from room temperature to a $-15°$ cold finger. During storage and fractionation some decomposition always occurred.

$(B_5H_8)_2CH_2$ was identified by its analysis and molecular weight. Elemental analysis was accomplished as previously described[2] after oxidation with fuming nitric acid or after hydrolysis with air-free water.

Anal. Calcd. for $(B_5H_8)_2CH_2$: C, 8.64; H (hydrolysis), 11.66; B, 78.24; mol. wt., 138.3. Found: C, 8.5; H, 11.65; B, 78.1; mol. wt. (gas density), 144; mol. wt. (cryoscopic, cyclohexane), 139. The melting point was 50.8–51.8° and the vapor pressure at 88° was 14 mm.

The infrared spectrum includes the major bands observed for B_5H_9[4] (2600, 1800, 1400, and 1100 cm.$^{-1}$). The 1800 cm.$^{-1}$ region exhibits two *well-defined* peaks which are found to be a characteristic of B_5H_9 derivatives substituted at the apex boron atom, when compared to compounds substituted at a base atom.[2,5,6]

The substance $(B_5H_8)_2CH_2$ reacts rapidly on exposure to air. Under vacuum, it decomposes very slowly at room temperature with evolution of a noncondensable gas, and the formation of liquid and a nonvolatile white solid with a B:C ratio of approximately 1:1.

The compound $(B_5H_8)CH_2BCl_2$ was more difficult to identify than $(B_5H_8)_2CH_2$ because of its lesser stability. It decomposes at room temperature and during vacuum transfers, producing HCl, a highly volatile boron compound, and a nonvolatile solid. Elemental analysis and molecular weight determination are in accord with the proposed formula.

Anal. Calcd. for $B_5H_8CH_2BCl_2$: C, 7.61; H (hydrolysis), 5.11; B, 41.11; mol. wt., 157.92. Found: C, 7.5; H, 5.2; B, 41.2; mol. wt. (cryoscopic, cyclohexane), 167. The infrared spectrum indicates the presence of C–H bonds, contains the main bands for B_5H_9 (including the twin peaks around 1800 cm.$^{-1}$ characteristic of apex substitution), and exhibits a strong broad band around 900 cm.$^{-1}$ which has been assigned to the B–Cl stretching mode.[7] These data and the method of synthesis prompt us to assign to the compound the structure II.

Both compounds, together with other substances such as CH_3BCl_2 and $B_5H_8CH_3$, were also found in low yields as products of the reaction of B_5H_9 with $CHCl_3$, $CHCl_2Br$, or CCl_4 in the presence of $AlCl_3$. In these instances, a carbon–halogen bond had been replaced by a carbon–hydrogen bond.

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[3] Nomenclature in accord with the preliminary report of the Advisory Committee on the Nomenclature of Boron Compounds, American Chemical Society.

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CONTRIBUTION FROM ROHM AND HAAS COMPANY,
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Isolation and Storage of Free Radicals on Molecular Sieves. II. The Electron Paramagnetic Resonance Spectrum of Nitrogen Difluoride (NF_2)

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A fairly well resolved, isotropic e.p.r. spectrum of NF_2 is obtained when $N_2F_4 \rightleftarrows 2\ NF_2$ is introduced above Linde Molecular Sieves 13X, 10X, and 5A at a pressure of 650 mm. and at room temperature. The NF_2 spectrum on 5A sieve, presented in Fig. 1, appears to show even better resolution than that obtained in solution.[1]

An F^{19} n.m.r. signal from adsorbed N_2F_4 is observed on the 13X and 10X sieves (effective pore diameters,

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