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.

[8] W. C. Bray and A. V. Hershey, *J. Am. Chem. Soc.*, **56**, 1889 (1934).
[9] J. Badoz-Lambling, *Bull. Soc. Chim. France*, 552 (1950).
[10] K. W. Sykes, *J. Chem. Soc.*, 124 (1952).

---

Contribution from the Chemical Technology Division,
Oak Ridge National Laboratory, Oak Ridge, Tennessee

## Hydrolysis of Neutron-Irradiated Uranium Monocarbide[1]

By M. J. Bradley, J. H. Goode, L. M. Ferris,
J. R. Flanary, and J. W. Ullmann

*Received December 5, 1963*

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.

[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
Laboratory of the Ohio State University,
Columbus 10, Ohio

## The Compounds $(B_5H_8)_2CH_2$ and $B_5H_8CH_2BCl_2$

By E. R. Altwicker, G. E. Ryschkewitsch,[1]
A. B. Garrett, and Harry H. Sisler

*Received December 16, 1963*

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

[1] Department of Chemistry, University of Florida, Gainesville, Florida.
[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).