creases with increase in the temperature of carbonization to a minimum in the residue obtained at 400°, rises to a maximum in the sample obtained at 800° and then decreases. With the low rank coal, the surface area decreases to a minimum at about 400°, rises to a small maximum at about 600° and then decreases to a second minimum at about 800°. The surface area of the 1000° char, however, is higher than that of the sample obtained at 800°.

The peculiar behavior observed with the low rank coal suggested that it might be due to a fine structure in the carbonized samples. Recent work at the British Coal Utilization Research Association<sup>2</sup> has shown that the cokes obtained at high temperatures exhibit an increase in surface area on oxidation. It was decided to investigate this phenomenon with the carbonized samples obtained from the coals mentioned above.

#### Experimental

The coals had the analyses indicated in Table I.

### TABLE I

#### Analysis of Coals

Ultimate % d.a.f.

Coal	Mois- ture, %	Ash, %	Car- bon	Hydro- gen	Nitro- gen	Sulfur (or- ganie)	Oxy- gen (by diff.)
Jharia (X	IV						
seam)	1.2	15.7	88.16	5.04	1.95	0.65	4.20
Raniganj	(Jamba	ad					
<b>D</b> 11	> 0 0	1 1 4	20 00	<b>F 00</b>	1 00	0 10	10 21

Bowlah) 8.0 15.4 79.00 5.39 1.68 0.42 13.51

The coals or chars were oxidized in a current of air until a loss in weight of about 11-15% occurred. The temperature and duration of oxidation are given in Table II. These data incidentally give a measure of the reactivity of the fuel, the low temperature coke or char being more reactive than the corresponding coal or the high temperature carbonization product. The surface area was measured as previously.<sup>1</sup>

### **Results and Discussion**

The BET surface areas of the original and the oxidized carbonization samples are presented in Table II. It is seen that there is a phenomenal increase in the surface area as a result of oxidation.

The important features of the study are: (1) the surface area after oxidation of the carbonization products obtained with the high rank coal decreases with increase in the temperature of carbonization of the parent sample; (2) the surface area after oxidation of the carbonization products obtained with the low rank coal, on the other hand, increases with increase in the temperature of carbonization of the parent sample; (3) the explanation given in the previous paper that the high reactivity of a low temperature coke or char is due to contributions from surface area and from the active groups is further confirmed. With the high rank coal, the surface area increases on oxidation with all the carbonized samples but the reactivity does not correspond to the increase in surface area. The low temperature char from the low rank coal which has the highest reactivity also has the lowest BET surface area. The results show that surface area by itself is not enough to explain reactivity and that other factors such as active groups also play their role. Investigations carried out at the Fuel Research Station<sup>3</sup> also have shown that there

(2) Brit. Coal Utilization Research Assoc. Quart. Gazette, 1957.

is no general relation between reactivity (toward steam) and surface area applicable to cokes made from different coals.

Walker and co-workers<sup>4–7</sup> have noticed a similar increase in surface area in the oxidation of carbons and Bastick, *et al.*,<sup>8</sup> in the gasification of cokes with carbon dioxide and water.

The above conclusions were based on results obtained with samples oxidized to the same percentage "burn off." It is possible the surface area at this "burn off" does not represent the maximum value. Further work is in progress to ascertain this factor.

## TABLE II

Reactivity and Surface Area (BET) of Cokes and Chars

Temp. of	Surfa	ce area								
carboni-	BET sq.	m./g. d.a.f.	Duration and	~ .						
zation,	Before	After	temp. of	% loss						
°С.	oxidation	oxidation	oxidation	in wt.						
Jharia coal										
Orig. coal	1.7	1.8	95 hr. (250°)	10.9						
500	2.0	234.6	0.5 hr. (400°)	10.5						
800	7.9	221.8	4.5 hr. (400°)	12.2						
1000	2.9	207.2	$10^{1}/_{4}$ hr. (400°)	15.2						
Raniganj coal										
Original	19.8	(i) <b>2</b> .5	(i) 148 hr. (200°)	13.8						
$\mathbf{coal}$	19.8	(ii) 178.8	(ii) 1.5 hr. (300°)	16.2						
400	1.3	99.9	1 hr. (300°)	14.6						
800	0.9	275.4	0.5 hr. (400°)	13.4						
1000	11.7	452.8	$2.5 \text{ hr.} (400^\circ)$	15.4						

(3) Fuel Research Board Ann Rep. London, p. 19 (1956).

(4) P. L. Walker, Jr., R. J. Foresti, Jr., and C. C. Wright, Ind. Eng. Chem., 45, 1703 (1953).

(5) P. L. Walker, Jr., and C. C. Wright, ibid., 45, 1715 (1953).

(6) P. L. Walker, Jr., F. Rusinko, Jr., and E. Raats, This JOURNAL, 59, 245 (1955).

(7) P. L. Walker, Jr., and F. Rusinko, Jr., *ibid.*, **59**, 241 (1955).
(8) M. Bastick, M. Montach and H. Guirin, *Compt. rend.*, **243**, 1764 (1957).

# FORMATION OF ETHYL ETHERATES OF DICHLOROBORANE AND DEUTERIODICHLOROBORANE

### BY T. ONAK, H. LANDESMAN AND I. SHAPIRO

Research Laboratory, Olin Mathieson Chemical Corporation, Pasadena, California

#### Received August 1, 1958

A recent investigation of the diborane-boron trichloride system in the dimethyl ether of diethylene glycol ("diglyme") indicated the formation of both mono- and dichloroborane etherates.<sup>1</sup> In studying this same system in ethyl ether we observed the preferential formation of the dichloroborane ethyl etherate. Results are based on infrared and B<sup>11</sup> nuclear magnetic resonance spectra which are reported here for dichloroborane etherate and deuteriodichloroborane etherate.

### Experimental

Boron trichloride gas (obtained from Matheson Co.) was fractionated through a 30 cm. glass helices packed column; infrared analysis indicated the presence of only trace amounts of phosgene. Diborane and deuterodiborane were prepared in the conventional manner as described pre-

(1) H. C. Brown and P. Tierney, J. Am. Chem. Soc., 80, 1552 (1958).

Standard high vacuum apparatus and techniques were used in the preparation and handling of all materials. The B<sup>11</sup> n.m.r. spectra were obtained by a Varian high resolution n.m.r. spectrometer operating at 12.8 mc. The infrared samples were prepared by placing a few drops of the liquid samples between two sodium chloride plates in a nitrogen filled dry box and spectra taken with a Perkin-Elmer Model 21 spectrophotometer.

In the preparation of dichloroborane ethyl etherate, a mixture of 10.00 mmole of ethyl ether, 3.72 mmoles of boron trichloride and 0.93 mmole of diborane was allowed to react at room temperature until all the diborane had been absorbed. Excess ether, 4.42 mmoles, was pumped off leaving dichloroborane etherate. Deuteriodichloroborane ethyl etherate was prepared in the same manner as described above for the dichloroborane etherate. The melting point of both etherates occurred in the range -27 to  $-23^{\circ}$ . The purity of both compounds was found to be better than 105% based on the stoichiometry of the reaction and n.m.r. and infrared analyses of the products. Difficulty was experienced in transferring dichloroborane ethyl etherate and etherate in the range of the melting point of the stoichiometry of the reaction and n.m.r.

Difficulty was experienced in transferring dichloroborane ethyl etherate and deuterodichloroborane ethyl etherate in the high vacuum system because of the low vapor pressures of the etherates. Dichloroborane etherate decomposed slowly at room temperature to give small amounts of ethane, diborane, ethyl chloride and boric oxide.

#### **Results and Discussion**

Using stoichiometric amounts of diborane, boron trichloride and ether, dichloroborane etherate was formed as

 $4\mathrm{BCl}_3 + \mathrm{B}_2\mathrm{H}_6 + 6(\mathrm{C}_2\mathrm{H}_5)_2\mathrm{O} \longrightarrow 6\mathrm{HBCl}_2(\mathrm{C}_2\mathrm{H}_5)_2\mathrm{O}$ 

In the infrared spectra dichloroborane etherate and deuteriodichloroborane etherate exhibit single absorption bands in the B-H(D) terminal stretching frequency region at 3.98  $\mu$  (B-H) and 5.31  $\mu$ (B-D), respectively. Also, dichloroborane etherate does not exhibit any absorption band in the B-H<sub>bridge</sub> frequency range.<sup>3</sup> Aside from the above mentioned infrared absorption and C-H band at 3.36  $\mu$  the remainder of the spectra for both compounds is complex.

On several occasions when excess diborane was used in the above reaction a small infrared absorbance was observed at slightly lower frequencies than the B-H (or B-D) stretching frequency in dichloroborane. This band, attributed to the BH<sub>2</sub> symmetric stretching of monochloroborane, disappeared on standing, leaving the spectrum of dichloroborane etherate.

The  $B^{11}$  n.m.r. spectrum of dichloroborane etherate exhibits only a symmetrical doublet, which is indicative of either a B-H unit or two nonequivalent boron atoms not bonded to hydrogen. The latter interpretation can be ruled out since the  $B^{11}$ -D spectrum of deuteriodichloroborane exhibits a singlet occurring midway between the two parts of the dichloroborane doublet. This

collapse of a B-H doublet by deuteration without observing any B<sup>11</sup>-D coupling already has been reported for deuterodecaborane.<sup>4</sup> Additionally, the separation of peaks for the dichloroborane etherate due to B<sup>11</sup>-H spin-spin coupling is found to be approximately the same as the analogous separation in pentaborane, again confirming the B-H unit assignment for the doublet.

(2) I. Shapiro, H. G. Weiss, M. Schmich, S. Skolnik and G. B. L. Smith, *ibid.*, **74**, 901 (1952).

(3) I. Shapiro, C. O. Wilson and W. J. Lehmann, J. Chem. Phys., 29, 237 (1958).

The  $B^{11}$  n.m.r. spectrum of boron trichloride etherate exhibits a singlet at a lower magnetic field than dichloroborane etherate. The expected spectrum of monochloroborane would be a triplet.

When diborane and boron trichloride in ether in varying proportions are mixed, only the singlet and/or the doublet are observed; no monochloroborane is detected. In contrast to this situation, evidence of a triplet in the n.m.r. spectrum due to monochloroborane is obtained when the "diglyme" solvent is used.

The fundamental structure (I) for dichloroborane etherate is implied by the above spectral studies.



Although the possibility of dimer, trimer, etc., formation is not ruled out, any such structure in which the boron atoms do not have the same chemical environment appears unlikely. Thus a dimer ( $[HBCl(OEt_2)_2]^+[HBCl_3]^-$ ) which is structurally similar to the diammoniate of diborane<sup>5</sup> is regarded as improbable. Likewise, dimers involving hydrogen bridging cannot be considered because there is no infrared absorption in the B-H<sub>bridge</sub> frequency range.<sup>3</sup>

Structure I could account for the observation that dichloroborane etherate decomposed to give small amounts of ethane, ethyl chloride and diborane. This decomposition is analogous to that of boron trichloride etherate, reported by Wiberg and Sutterlin to give ethyl chloride.<sup>6</sup> The formation of ethane and diborane in the former case is not surprising in view of the presence of the hydridic hydrogen.

Acknowledgment.—The authors appreciate the assistance given by Drs. R. E. Williams and W. J. Lehmann in the preparation and interpretation of the n.m.r. and infrared spectra.

(4) R. E. Williams and I. Shapiro, ibid., 29, 677 (1958).

(5) S. G. Shore and R. W. Parry, J. Am. Chem. Soc., 77, 6084 (1955);
 D. R. Schultz and R. W. Parry, *ibid.*, 80, 4 (1958).

(6) Wiberg and Sutterlin, Z. anorg. allgem. Chem., 202, 21 (1931).

## THE MOLAR REFRACTION OF METHYL ISOCYANATE

### BY WILLIAM M. TOLLES AND JEROME R. TICHY<sup>1</sup>

Contribution from the Department of Chemistry, The University of Connecticut, Storrs, Connecticut

Received August 7, 1958

In connection with another problem, the occasion arose to prepare some methyl isocyanate. A search of the literature indicates the physical constants of this compound are not well established. Aside from the b.p.  $43-45^{\circ}$ , no values exist for the density or refractive index.

We have determined these latter constants and found them to be  $n^{27}$ D 1.3630 and  $d^{27}$ 4 0.9230. With these values, the molecular refraction is found to be 13.73. The molecular refraction calculated for CH<sub>3</sub>NCO is 13.68 while that for CH<sub>3</sub>OCN is

(1) Maine Medical Center, 22 Bramhall St., Portland, Maine.