this Laboratory[8] since the death of Professor Underwood. We have repeated and checked the preparation and properties of "phenoldiphenein" and its dimethyl ether, m. p. 150.5–151.5° uncorr. (according to Underwood) and the preparation of 2,2'-dianisoylbiphenyl, m. p. 150–151.4° uncorr. (according to Bachmann). We have also made a direct comparison of the so-called "phenoldiphenein lactone dimethyl ether" and the 2,2'-dianisoylbiphenyl by the method of mixed melting points and find that no depression occurs (mixed m. p. 150–151°). In view of the fact that all the positive experimental evidence brought forward to support the unsymmetrical formulation is equally applicable to the symmetrical type and particularly in view of the insolubility of the "lactone" in alkali, the yellow color of alkaline solutions of "phenoldiphenein," and the great dissimilarity of their absorption spectra from those of phenolphthalein, the results of the direct comparison reported here for the first time appear to assure the validity of the symmetrical or diketone formulation (II).

While our work was in progress Bell and Briggs[9] also confirmed Underwood's preparation of "phenoldiphenein" and its dimethyl ether. In addition they prepared 2,2'-dianisoylbiphenyl by interaction of diphenic acid chloride with anisole in the presence of aluminum chloride. Bell and Briggs, however, gave no indication that they were aware of Bachmann's previous synthesis of this compound. Moreover, since their method did not eliminate the possibility that the aluminum chloride might have caused rearrangement of the symmetrical diphenic acid chloride to an unsymmetrical form analogous to that well known for phthalyl chloride,[10] their preparation may not by itself be regarded as *proof* of the symmetrical structure. Furthermore, they reported no direct comparison of their "phenoldiphenein dimethyl ether" and their 2,2'-dianisoylbiphenyl. In other words, Bell and Briggs' statement that these two compounds are identical is correct, but the evidence for it is contained solely in the combination of Bachmann's work with our own direct comparison of the Underwood and Bachmann products. Bell and Briggs' report now, however, becomes evidence that in the Friedel–Crafts

(8) Carten, S.B. Thesis, 1936; Moos, M.S. Thesis, 1937; Moos, Ph.D. Thesis, in progress.

(9) Bell and Briggs, *J. Chem. Soc.*, 1561 (1938).

(10) Ott, *Ann.*, **392**, 273 (1912); "Organic Syntheses," **11**, 88 (1931).

condensation with anisole diphenic acid chloride does react in the symmetrical form.

With Underwood's "phenoldiphenein lactone dimethyl ether" thus established as in fact 2,2'-dianisoylbiphenyl, the question arises whether Dutt's compound may not have been the true phenoldiphenein. We are continuing our experiments on the preparation of the latter by an independent method.

Non-Reaction of Ethylene Oxide and Methanol

BY J. LESLIE JONES

In an effort to obtain an example of a gaseous bimolecular association reaction, the writer studied the possible reaction between ethylene oxide and methanol to form monomethyl ether of ethylene glycol. Purified and dried samples of the gases were mixed under the usual conditions for the study of reaction kinetics. There was no evidence of an association reaction (resulting in pressure decrease) for temperatures up to 350° and over a period of four hours. An ethylene oxide pressure of 125 mm. and 200 mm. of methanol were typical of the concentrations employed. In order to determine whether a comparatively rapid reaction was occurring, 112 mm. of ethylene oxide and 154 mm. of methanol were mixed at 183° and the temperature of the thermostat gradually raised to 342°; the final pressure was within one mm. of the calculated pressure based upon no reaction. A similar experiment was tried at 181° employing 163 mm. of ethylene oxide and 142 mm. of purified *t*-butyl alcohol and heated for ninety minutes. No pressure change was detected. There was no evidence of acetaldehyde or acetone in the reaction products of the methanol experiments, thus excluding, respectively, the isomerization of ethylene oxide or the formation of a hemi-acetal. There was a definite increase in the pressure of pure ethylene oxide on standing at 342° for 10.5 hours (from 100 to 131 mm.).[1]

Fletcher and Rollefson reported that ethylene oxide catalyzed the decomposition of methanol at 465° (pure methanol is stable at 465°). Heckert and Mack reported a rapid reaction between gaseous ammonia and ethylene oxide at room tempera-

(1) Heckert and Mack, THIS JOURNAL, **51**, 2706 (1929); Fletcher and Rollefson, *ibid.*, **58**, 2135 (1936); Thompson and Meissner, *Trans. Faraday Soc.*, **32**, 1451 (1936).

ture. Altman and Kedrinskii[2] reported a reaction between ethylene oxide and ethanol in the presence of $H_2SO_4·H_2O$ as a catalyst at room temperature and atmospheric pressure, with 70% yield of ether in three hours. Brönsted, Kilpatrick and Kilpatrick[3] studied the kinetics of the hydrolysis of ethylene oxide in aqueous solution and found the reaction to proceed mainly as a basically catalysed reaction.

A very small steric factor accompanied by a comparatively high value of the activation energy would account for the present results. The work of Altman and Kedrinskii indicated a predominantly ionic mechanism for the liquid phase reaction. A very small steric factor for the gas phase reaction is in agreement with the deductions of Bawn concerning association reactions.[4] Apparently the formation of ether derivatives of ethylene oxide must occur through an ionic mechanism, in order to account for the rates of reactions in the liquid phase at room temperatures, or as heterogeneous reactions.

(2) Altman and Kedrinskii, Trans. Exptl. Research Lab. Khemgas, Materials on Cracking and Chemical Treatment of Cracking Products, U. S. S. R., 3, 34 (1936).
(3) Brönsted, et al., THIS JOURNAL, 51, 428 (1929).
(4) Bawn, Trans. Faraday Soc., 31, 1536 (1935).

HOWARD UNIVERSITY
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Note on the Adsorption of Gases by Graphite. II

BY ARTHUR B. LAMB AND EDWIN N. OHL

Recently,[1] in connection with the study of the adsorption of gases by graphite, data were presented showing that at 0° and at −195.2° hydrogen is adsorbed much less by the pure graphite formed as pseudomorphs on heating crystalline silicon carbide to a very high temperature, than it is on ordinary Acheson graphite. Thus, at 300 mm. pressure and −195.2°, the adsorptions were 0.83 ± 0.01 on Acheson graphite and 0.18 ± 0.01 cc. per gram on the pseudomorphs, the ratio being 4.6 ± 0.3. In this connection it was also stated that the adsorptions of dichlorodifluoromethane (Freon) and of carbon dioxide at 0° on these pseudomorphs "were so slight as to be no greater than our errors of observation."

These very slight adsorptions of dichlorodifluoromethane and of carbon dioxide were somewhat surprising because these gases had been found to be moderately adsorbed on Acheson

(1) Lamb and Ohl, THIS JOURNAL, 60, 1287 (1938).

graphite at 0° (0.96 ± 0.02 cc. of CCl_2F_2 and 0.17 ± 0.01 cc. of CO_2 per gram at 300 mm.) so that on the basis of the above ratio (4.6) of the adsorptions of hydrogen on these two varieties of graphite, a small but nevertheless measurable adsorption on the graphite from silicon carbide would have been expected. However, as this anomaly appeared to have no important bearing on our main thesis it was not studied further.

Dr. P. H. Emmett has now in a private communication kindly called attention to these surprisingly small adsorptions and has also pointed out that if these gases were indeed so very slightly adsorbed by the graphite from silicon carbide, it might be argued plausibly that the observed, relatively large adsorption of *hydrogen* on this graphite was due to the presence in it of some extra porosity, accessible to hydrogen but not to dichlorodifluoromethane or carbon dioxide, which is not present in Acheson graphite; an inference exactly contradictory to our conclusion based on other evidence.

In view of this possible inference we have re-examined our measurements of the adsorption of these gases on the graphite from silicon carbide. We find that the results obtained in these measurements were unusually irregular, those with dichlorodifluoromethane being particularly so, and for no apparent reason. The adsorptions observed with carbon dioxide were indeed small but were clearly greater than the experimental error.

In the hope of securing more definite evidence in this matter we have now repeated these measurements with especial care on a fresh sample of the pseudomorphic graphite derived from silicon carbide. The new data are in general agreement with those previously obtained but are far less erratic. They are shown graphically in Fig. 1 along with comparable data given previously[1] for carbon dioxide and Freon at 0° on ordinary Acheson graphite.

It can be seen from curves No. 2 and 4 of the figure that the adsorptions of these gases, while small, are by no means negligible, being 0.22 ± 0.01 cc. for Freon and 0.032 ± 0.01 cc. for carbon dioxide, at 300 mm. pressure. These adsorptions, compared with the corresponding values for these gases on Acheson graphite given above, yield the ratio 4.4 ± 0.3 and 5.2 ± 0.5, respectively. These ratios are practically identical with the ratio obtained for hydrogen on these two varieties of graphite at −195.2° and 300 mm. pressure, so